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Destroying Chemical Wastes in Commercial Scale Incinerators. Facility Report Number 3 - Systems Technology

TRW Defense and Space Systems Group, Redondo Beach, Calif

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Incineration tests of selected chemical wastes were conducted at the fluidized bed incinerator facility operated by Black Clawson Fibreclaim, Inc., in Franklin, Ohio. These tests were performed under contract with Systems Technology Corporation to determine the effectiveness of thermal destruction of two different industrial liquid wastes: 1) an aqueous phenol sludge, and 2) an aqueous solution of methyl methacrylate monomer. Each waste was burned at two different conditions to determine the effects of normal operating and equipment variables. Analysis of combustion gas samples indicated destruction efficiencies of over 99.999 percent for each waste consitituent. Standard EPA Method 5 tests were performed on stack emissions to determine particulate loading and composition. No organics were detected in the scrubber water or ash. Test results indicated that either waste can be effectively destructed in a fluidized bed reactor. Estimated cost of destroying 13.2 million liters/year of aqueous methyl methacrylate was $6 million capital investment and an operating cost of $255/metric ton. Cost of incinerating 23.8 million liters/year of aqueous phenol waste was estimated to be $6 million capital investment and $124/metric ton operating cost.

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DESTROYING CHEMICAL WASTES IN COMMERCIAL-SCALE INCINERATORS

Facility Report No. 3

This final report (SW-122c) describes work performed
for the Federal solid waste management program
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FOREWORD

The tests described in this report are part of a program designed to evaluate the environmental, technical, and economic feasibility of disposing of industrial wastes via incineration. This objective is being pursued through a series of test burns conducted at commercial incinerators and with real-world industrial wastes. Approximately eight incineration facilities and seventeen different industrial wastes will be tested under this program. The incineration facilities were selected to represent the various design categories which appear most promising for industrial waste disposal. The wastes were selected on the basis of their suitability for disposal by incineration and their environmental priority.

This report describes the test conducted at Systems Technology (Franklin, Ohio), which was the third facility of the series. Facility reports similar to this one have been published for the first two tests which were conducted at the Marquardt liquid injection facility in Van Nuys, California, and the Surface Combustion pyrolysis facility in Toledo, Ohio. The facility reports are primarily of an objective nature presenting the equipment description, waste analysis, operational procedures, sampling techniques, analytical methods, emission data and cost information. Facility reports are published as soon as possible after the testing has been completed at a facility so that the raw data and basic results will be available to the public quickly.

In addition to the facility reports, a final report will also be prepared after all testing has been completed. In contrast to the facility reports which are primarily objective, the final report will provide a detailed subjective analysis on each test and the overall program.

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1. SUMMARY

Incineration tests of selected chemical wastes were conducted at the fluidized bed incinerator facility operated by Black Clawson Fibreclaim, Inc., in Franklin, Ohio. These tests were performed under contract with Systems Technology Corporation to determine the effectiveness of thermal destruction of two different industrial liquid wastes: 1) an aqueous phenol sludge, and 2) an aqueous solution of methyl methacrylate monomer. Each waste was burned at two different conditions to determine the effects of normal operating and equipment variables.

The phenol sludge contained 86 percent water and 5.5 percent ash with the remaining organic portion consisting mainly of phenol and cresols. The wastes elemental composition was approximately 6 percent carbon and 10.5 percent hydrogen. Nitrogen, sulfur, and halogen (as chlorine) levels were relatively low at 0.1, 0.5, and 0.07 percent, respectively. The major inorganic components of the ash were S, Na, Fe, Ca, Si, Al, K, Mg, and P. Heat content of the phenol sludge could not be determined due to the high water content, but is probably less than 1500 kcal/kg.

The methyl methacrylate waste also had a high water content, 38 percent water, and contained approximately 2 percent ash. The aqueous phase and the organic phase, which is almost entirely the monomer, tend to separate on standing and vigorous mixing is required to keep the waste homogeneous. The waste was composed of about 38 percent carbon, 9.5 percent hydrogen, and 0.7 percent halogens (as chlorine) with only traces of nitrogen and sulfur at 600 ppm and 800 ppm, respectively. The major inorganic components of the ash were Na, S, Ti, Al, Ca, Pb, Si, Mg, and P. Heat content could not be measured on this waste either and is similarly believed to be less than 1500 kcal/kg.

The fluidized bed incinerator utilized for testing is of commercial design and capacity. The reactor is 7.6 meters in diameter by 10 meters high, and has an input feed rate of over 1000 liters per hour. Auxiliary fuel can be injected simultaneously with low heat content wastes to support combustion when required. Reactor bed operating temperature range is 650 to 1050°C. The incinerator is equipped with a Venturi scrubber and mist separator which remove up to 98 percent of the particulate and reduce the stack exhaust gas temperature to 82°C.

Test burn operating conditions for each waste are summarized in Table 1-1, beginning with the range of test conditions for each waste, including bed and freeboard temperatures, residence time, waste feed rate, and waste/auxiliary fuel ratio. The ratio of waste feed rate to auxiliary fuel feed rate was utilized as the test variable for each waste. A baseline test with auxiliary fuel only was performed to obtain background emissions data. Auxiliary fuel (Number 2 oil) was required to destruct these wastes because of the water content: 86 percent water in the phenol waste and 38 percent water in the methyl methacrylate waste.

Table 1-1. Results Summary

	Phenol Waste	Methyl Methacrylate
Bed Temperature, Average (°C)	740-757	774-788
Freeboard Temperature (°C)	813-899	824-843
Residence Time (sec)	12-14	12
Waste Feed Rate (1/min)	34-50	30-36
Waste/Auxiliary Fuel* (1/1)	2.3-3.0	2.0-2.6
Quality of Stack Emissions		
Particulate (mg/m^3)	1280-1430	560-630
Trace Metals (mg/m^3)	0.44-0.87 Pb	0.55-2.2 Pb
Quality of Combustion Gas:		
Total Organics (mg/m^3)	7.0-7.6	7.5
Waste Content (mg/m^3)	Not Detected (<0.03)	Not Detected (<0.16)
Trace Metals (mg/m^3)	1.0-1.2 Pb	0.85-4.7 Pb
Quality of Scrubber Water:		
Total Organics (mg/1)	Not Detected (<0.4)	Not Detected (<0.2)
Trace Metals (mg/1)	0.50-2.7 Pb	0.45-1.8 Pb
Quality of Ash (Fluidizing Sand):		
Waste Content (mg/kg ash)	Not Detected (<0.2)	Not Detected (<1.0)
Destruction Efficiency:		
Total Organics (percent)	99.97-99.98	99.99
Waste Constituents (percent)	>99.999	>99.999
Capital Cost ($)	6,075,200	5,984,200
Operating Costs ($/metric ton)	125	255
Plant Size (1/yr)	22.7 million	13.2 million

*No. 2 oil utilized as auxiliary fuel for all tests

Particulate loadings up to 1430-mg/m^3 were measured in the stack gases. Most of the particulate consisted of fine sand particles disintegrated from the fluidizing bed by direct injection of these high water content wastes. Since both of the wastes tested contained lead, trace metal analyses indicated the presence of lead in the combustion gases, stack emissions, and scrubber water. Scrubber water analysis did not indicate the presence of any organic material above the detection limits noted in Table 1-1. No waste constituents were found in the fluidizing sand samples, above the detection limits of the analysis.

Incineration of each waste was accomplished with high efficiencies in the fluidized bed reactor, as indicated in Table 1-1. Waste destruction efficiencies were over 99.999 percent for each test. The total organic destruction efficiencies were 99.97 to 99.99 percent. Destruction efficiency for total organics compares the input rate of combined waste and auxiliary fuel to emitted rate of all organic material found in the combustion zone samples. Waste destruction efficiency compares only waste input rate to concentration of organic waste constituents in the combustion gas. All samples were taken at the combustion zone exit prior to the scrubber system. A sample destruction efficiency calculation is presented in Appendix C. In addition to the fact that the waste constituents could not be detected in the combustion gas (less than 01. mg/m^3), no significant evidence of any toxic by-products of the waste destruction, such as polynuclear organic material (POM) was found.

Capital and operating cost estimates were prepared for fluidized bed reactor-venturi scrubber systems to destruct each of the two wastes. Capital investment, not including land costs, for a facility to incinerate 13.2 million liters/yr of aqueous methyl methacrylate is approximately six million dollars, with an operating cost equivalent to $255/metric ton of waste destructed. A facility to incinerate 23.8 million liters/yr of aqueous phenol waste would also require a capital investment of six million dollars, less land costs, and an operating cost of $124/metric ton.

2. INTRODUCTION

The objective of this facility test program is to evaluate the effectiveness of thermally destructing specific industrial chemical wastes in an existing commercial scale processing facility. These facility tests are part of an overall U.S. Environmental Protection Agency sponsored program involved with selective testing of sixteen different wastes at seven generic types of thermal destructing facilities. The purpose of the test program is to acquire useful disposal technology as well as economic information. This report describes test operations and results of incinerating two different liquid wastes, phenol and methyl methacrylate, in a 7.6-meter diameter, commercial, fluidized bed incinerator at Franklin, Ohio, under contract with Systems Technology Corporation (Systech).

The Systech Waste Treatment Center is adjacent to the Franklin Solid Waste and Fiber Recovery Plant, operated by Black Clawson. Systech has an exclusive contract with Black Clawson for the destruction of liquid wastes in the fluidized bed reactor. This plant was designed and constructed under a Demonstration Grant from the Office of Solid Waste Management Programs, U.S. Environmental Protection Agency. In continuous operation since 1971, the plant has met the complete waste disposal requirements of the city of Franklin.

This fluidized bed reactor was selected for the program as a modern, well-instrumented incinerator of commercial capacity and design. Manufactured by Dorr-Oliver, the unit has an input feed rate of up to 1,360 liters per hour of high heat content liquids (over 5,560 kcal/kg) and up to 7,570 liters per hour of liquids with a heat content of 1,670 kcal/kg. Municipal wastes are burned at a maximum rate of 135 metric tons in 24 hours Heat release capability is 15 million kcal/hr. The fluidized bed system is equipped with a venturi scrubber to control particulate emissions.

The two wastes tested at the Systems Technology facility, an aqueous methyl methacrylate monomer waste and an aqueous phenolic waste, were selected on the basis of their suitability for the fluidized bed reactor. The methyl methacrylate waste is a flammable, green-black liquid. Its vapor is heavier than air and may travel a considerable distance to a source of ignition and flash back. Also, at elevated temperatures, such as in fire conditions, polymerization may take place. For these reasons, the fluidized bed incinerator, with its nearly isothermal conditions and lower operating temperature, is ideal for the destruction of the methyl methacrylate waste. The aqueous phenol waste is a black, thick liquid with a large volume of suspended solids and contains over 85 percent water. The fluidized bed incinerator was selected for the destruction of the aqueous phenol waste because of (1) its ability to handle suspended solids, and (2) its lower operating temperature resulting in lower thermal energy requirement for converting the water contained in the waste to steam at the incineration temperature. An additional consideration was that both the aqueous methyl methacrylate waste and the aqueous phenol waste were readily available at the Systems Technology facility.

The methyl methacrylate waste is generated from the manufacture of acrylic plastic material, such as Lucite and Plexiglas. Methyl methacrylate wastes are also generated from the manufacture of surface-coating resins, such as latex paints, lacquer resins, and enamel resins. The phenol waste is generated from the scrubbing of gasoline with caustic to remove hydrogen sulfide and phenol, and is a major waste stream from petroleum refineries. Because of the size of the acrylic plastic and the petroleum refining industries, both the methyl methacrylate waste and the phenol waste are generated in large quantities. It is estimated that the methyl methacrylate waste is generated at the rate of 1 to 10 million kg per year, whereas the phenol waste is generated at the rate of over 50 million kg per year.

Two months after completion of these tests, Systech stopped incinerating liquid industrial wastes in the fluidized bed reactor, at Black Clawson's request. This request was made because some of Systech's wastes caused operating problems which included:

- Disintegration of the sand bed, apparently due to the thermal effect of injecting liquid directly into the bed.
- Abnormal buildup of multilayered, multicolored crust on the wall of the reactor in the vicinity of the freeboard/bed interface.
- Buildup of ash of an abnormal physical character in the duct work leading from the reactor to the scrubber.
- Defluidization of the bed due to agglomeration and to contamination by chunks of the deposits described above.

Systech believes that defluidization of the bed or abnormal crust or ash buildup would not develop during the incineration of the wastes tested during this program. Some depletion of the bed sand was observed during these tests, however, during which high water content wastes were injected directly into the bed.

The following report sections describe in detail the incinerator process equipment (Section 3), and the waste destroyed and test and sampling procedures followed (Section 4). Test results are presented and discussed (Section 5), including effectiveness of destruction of the wastes. An estimate of the capital investment and operating costs of disposing of wastes using this type of incinerator equipment is also included in the report (Section 6).

3. PROCESS DESCRIPTION

3.1 FACILITY PROCESS

The fluidized bed reactor facility process is shown schematically in Figure 3-1. Basic system components include:

- Fluidized bed reactor
- Fluidizing air blower
- Waste feed system
- Auxiliary fuel feed system
- Instrumentation
- Emission control system

Following is a description of the incinerator and feed systems. Facility instrumentation and emission controls are discussed in subsequent Sections 3.2 and 3.3, respectively.

3.1.1 Fluidized Bed Reactor

The top of the fluidized bed reactor is shown in Figure 3-2. Manufactured by Dorr-Oliver, the reactor has an inside diameter of 7.6 meters and an elevation of 10 meters. The silica bed is 1 meter deep at rest, extending up to 1.8 meters in height when fluidizing air is passed through the bed. Waste and auxiliary fuel are injected radially into the bed and reacted at temperatures from 600° to 810°C. Further reaction occurs in the reactor freeboard volume above the bed at temperatures up to 980°C. Construction is of carbon steel with refractory lining.

Maximum heat release of the reactor is 15 million kcal/hr. Input feed rate is up to 1,360 liters per hour of liquids over 5,560 kcal/kg heat content, and up to 7,570 liters per hour of liquids with a heat content of 1,670 kcal/kg. Municipal wastes are combusted at a maximum rate of 135 metric tons in 24 hours.

3.1.2 Air Supply System

A fluidizing air blower (Figure 3-1) powered by a 225 kilowatt (300 horsepower) electric motor provides a maximum of 440 m^3/min of air to fluidize the bed. Additional combustion air of up to 115 m^3/min is supplied to overbed air nozzles by the same blower. The reactor preheat burners have a separate air supply blower, as shown in Figure 3-1.

3.1.3 Waste Feed System

Liquid wastes were pumped directly from a tank truck into the reactor by a recirculating pump system supplied by Systech, and not part of the system shown in Figure 3-1. Wastes were injected radially into the reactor bed through a single 9.5 mm diameter nozzle. Flow rates were determined by recording waste liquid level changes in the calibrated tanker as a function of time.

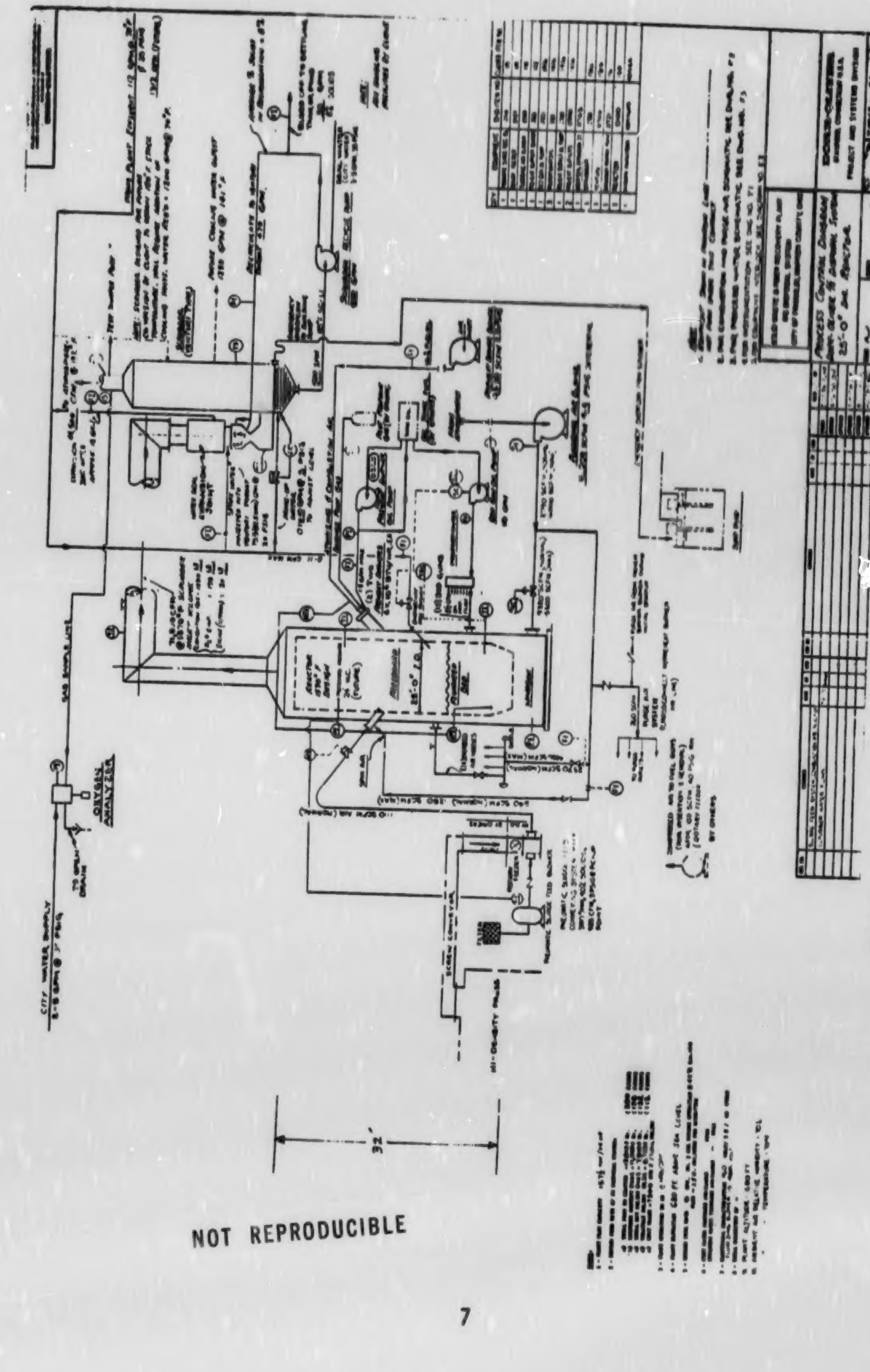

Figure 3-1. Facility Process Flow Schematic Diagram

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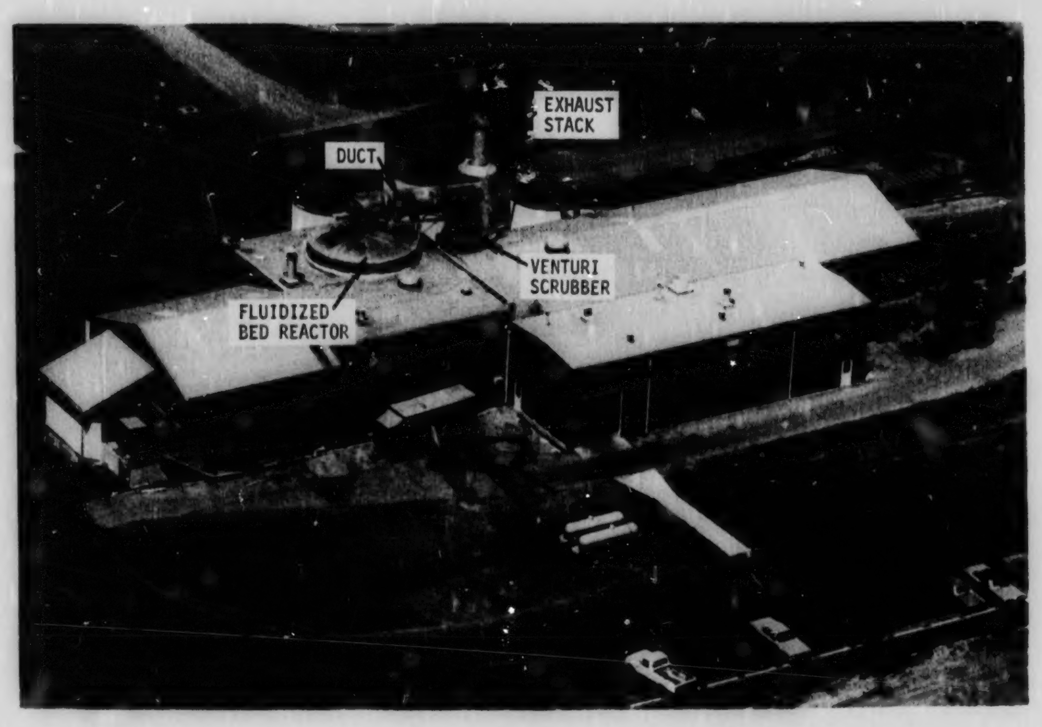

Figure 3-2. Overall View of Facility

3.1.4 Auxiliary Fuel Feed System

Auxiliary fuel (No. 2 fuel oil) was fed radially into the bed through 10 bed nozzles manifolded around the reactor circumference. A maximum of 18 bed guns are shown in Figure 3-1, but this number is not normally used. Fuel oil flow was measured by a flow totalizer (total volume meter) in the feed line, and verified by recording oil tank liquid level versus time.

3.2 INSTRUMENTATION

Instrumentation capability provided at this facility for the test program is shown in Figure 3-3. Instruments were calibrated by Black Clawson personnel prior to initiation of testing. Measurements were made of all process parameters, including pressures, temperatures, and flow rates. On line measurement of oxygen content in the exhaust stack was also conducted. Additional on line gas analysis instruments were monitored in the TRW sampling trailer. The main facility instrumentation and control panel are shown in Figure 3-4.

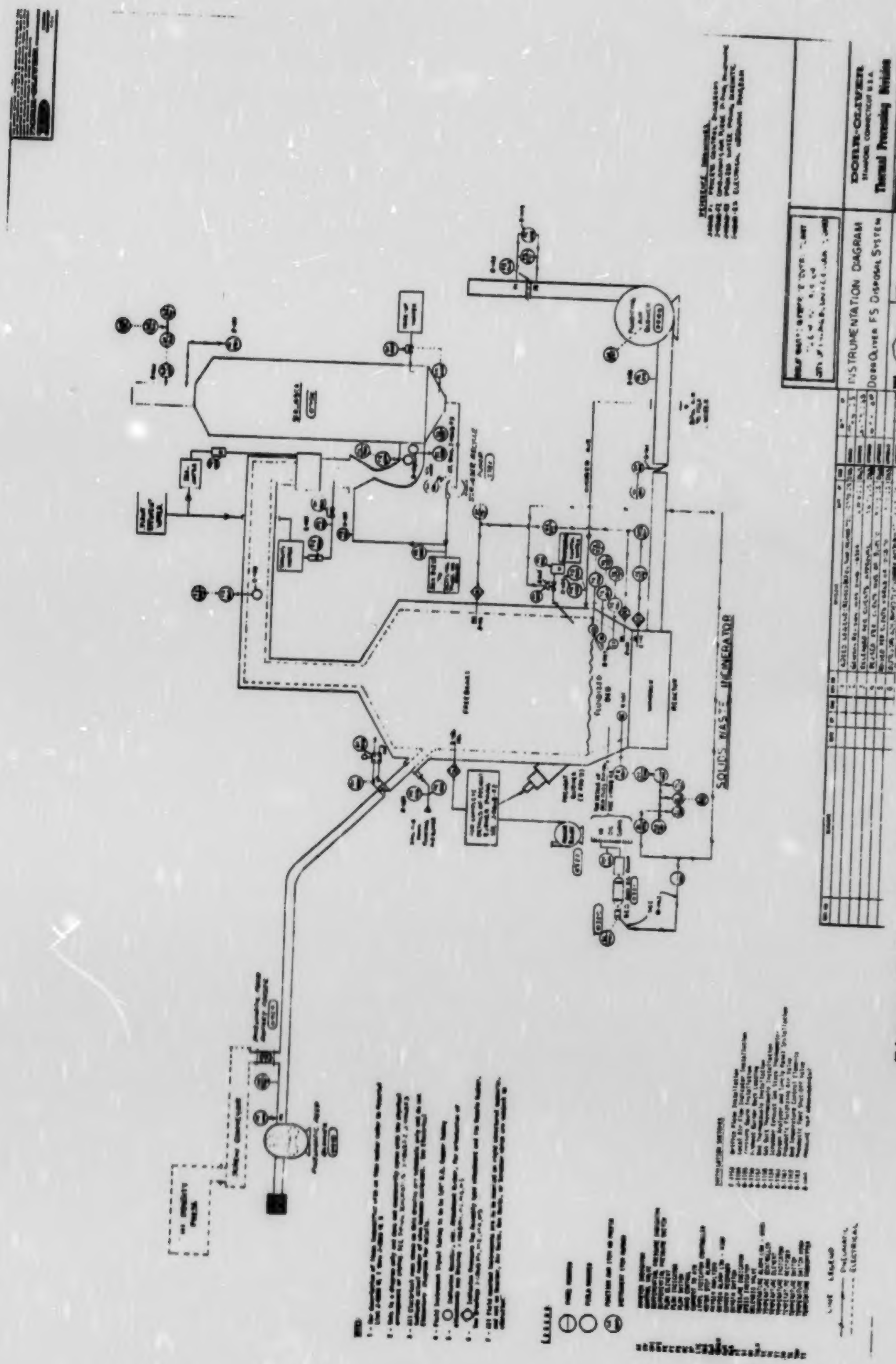

Figure 3-3. Facility Instrumentation Schematic Diagram

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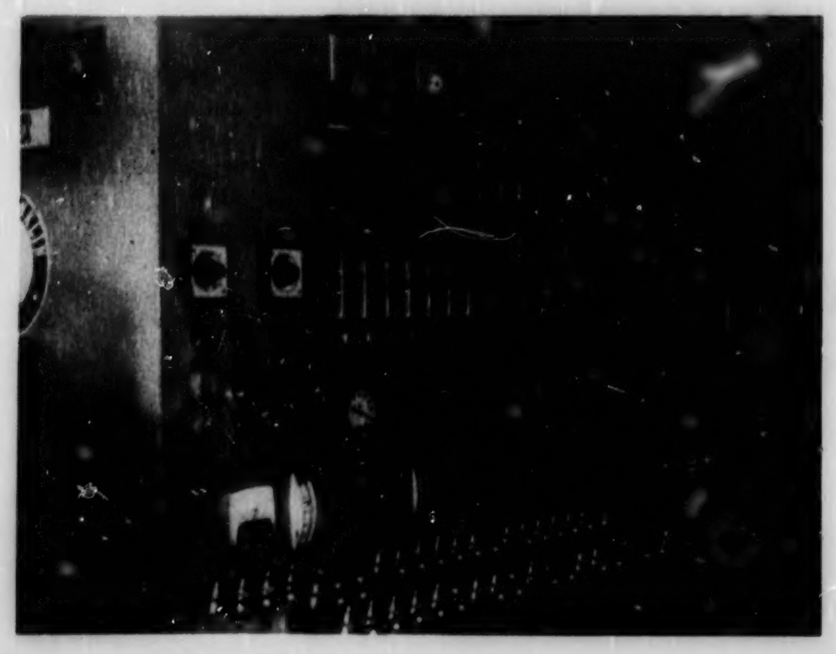

Figure 3-4. Main Facility Instrumentation and Control Panel

3.3 EMISSION CONTROLS

Atmospheric emissions from the combustion of liquid wastes during the Systech incineration tests were controlled by a venturi scrubber, shown in Figure 3-1. The top of the scrubber can also be seen in Figure 3-2. Recirculating water is injected into the venturi to scrub particulate matter from the combustion gas stream and quench the gas temperature from ∿820° to ∿80°C prior to emission into the atmosphere through the stack. Spent scrubber liquid is sent to the Miami Conservancy District Wastewater Treatment Plant (adjacent to the incinerator) for processing.

4. TEST DESCRIPTION

This section presents the manner in which the tests were carried out. It is divided into the following subsections, listed in order of discussion:

- Physical and chemical description of the wastes that were tested
- Operational procedures used and a test-by-test commentary
- Sampling methods
- Analysis techniques
- Description of the problems encountered related to the facility and sampling.

4.1 WASTES TESTED

The two wastes selected for testing at Systech were from processes using phenol and methyl methacrylate (MMA). Survey samples were obtained as early as possible before the tests and representative samples were taken at Systech from the waste-containing tank trucks at the start of each test day. The character of both of these wastes changed noticeably from the survey to the representative samples. The survey sample of the phenol waste contained so much solids (~13 percent) that it poured in lumps. However, the representative sample had a smooth consistency and much lower solids content. The survey sample of the MMA waste was a high heat content material of almost pure monomer (~98 percent), whereas the representative sample was a highly watered waste stream. Thus, most of the analyses performed on the survey samples had to be repeated and the results reported in this section, except as noted, are from the representative waste samples. The analyses used to characterize the wastes and to determine the expected compounds of interest in the test burn samples were:

- Thermal content
- Viscosity
- Specific gravity
- Loss on ignition (LOI)
- Percent water
- C,H,N,S, and halogens
- Infrared spectroscopy (IR)
- Low resolution mass spectroscopy (LRMS)

- Combined gas chromatography/mass spectroscopy (GC/MS)
- Spark source mass spectroscopy (SSMS)

The results from these analyses are discussed in the following sections.

4.1.1 Phenol Waste

The phenol waste was a greenish-black opaque liquid with a large amount of suspended solids. It had a strong phenol odor with an accompanying odor resembling that of crude oil. Neither heat content or viscosity could be measured on this waste. The waste would not ignite in the calorimeter due to its high water content and its high solids loading interfered with viscosity measurements. The waste had a specific gravity at 15°C of 1.0623, an LOI of 94.5 percent, and was determined to be 86 percent water.

Elemental analyses performed showed the composition of the waste to be:

carbon — 5.9 percent
hydrogen — 10.5 percent
nitrogen — 0.10 percent
sulfur — 0.5 percent
halogens as chlorine — 0.07 percent

4.1.1.1 Organic Composition

The organic portion, that part of the representative waste which was not water or solids (as determined by LOI), consisted of about half phenol with cresols and substituted benzenes making up most of the remaining organics. The concentration of the organic constituents in the waste, as determined by GC/MS using the total ion monitor for normalized quantitation is shown in Table 4-1. The composition of the representative sample is essentially the same as the survey sample (Reference 1), except that the ethanol, acetone, 2-butanone, butanol, and 2-ethoxyethanol were not present in the survey sample.

A survey analysis by IR and LRMS was performed on the representative sample of the phenol waste to look for organic species not necessarily detected in the other analyses. An aliquot of the representative phenol waste sample was evaporated in air at approximately 50°C to remove the water and some of the volatile compounds already quantified by GC. The resulting spectra were clearly indicative of phenol as the major constituent. Most of the peaks can be assigned to phenol. Certain broad areas of absorption, 1400 to 1500 cm^{-1}, are attributed primarily to p-cresol also being present in the sample. There were no indications of any other species being present. The IR normally does not indicate a compound's presence at levels below 5 percent weight composition in the sample. The LRMS spectral patterns obtained from the samples at sample probe temperatures from 50° to 400°C indicated the presence of the constituents phenol,

Table 4-1. Organic Composition of Phenol Waste Representative Sample

Compound	Estimated Level in the Waste Sample (Percent w/w)[a]
Ethanol	0.06
Acetone	0.07
2-Butanone (MEK)	0.05
Butanol	<0.01
2-Ethoxyethanol	0.07
Toluene	0.3
Xylene (two isomers)	0.6
Isopropyl benzene	0.8
Phenol	3.7
o-Cresol	0.9
m-Cresol	1.9

[a] Sample contained 86 percent water and approximately 5.5 percent nonignitable solids.

cresols, and aliphatic and unsaturated hydrocarbon oils. Spectral assignments can be found in Table D-7 in the appendix.

There was also strange evidence of either one or perhaps both of two classes of compounds: (1) methyl esters of various different carboxylic acids, and (2) sulfur containing hydrocarbons such as sulfides, dithianes and trithianes. These materials were not seen in the GC/MS analysis of these samples (Table 4-1) and are believed to be of low enough volatility so as to not elute from the chromatographic columns. The sulfur containing hydrocarbons could account for some of the 0.5 percent sulfur found in the elemental analysis.

4.1.1.2 Trace Elements

Trace elemental analysis was performed by SSMS. This analysis showed the major species to be sulfur, sodium, and iron. The concentrations of the other elements detected down to 0.1 ppm as well as all toxic elements are presented in Table 4-2. The corresponding concentrations of these elements in the resulting combustion gas have been calculated based on average fuel and air feed conditions at Systech and are also included in this table. The SSMS data are typically accurate within 500 percent and should thus be regarded only as estimates. For this reason, and also because its volatility makes it extremely difficult to detect by SSMS,

Table 4-2. Trace Metals in the Phenol Waste

Element	Approximate Concentration in Waste (ppm)	Calculated Theoretical Concentration in Combustion Gas (mg/m^3)
Ca	310	26
Si	240	20
Al	86	7.3
K	75	6.4
Mg	40	3.4
P	33	2.8
Pt	16	1.4
Ti	15	1.3
Sn	6	0.5
Zn	6	0.5
V*	5	0.4
Cr*	4	0.3
Cu	4	0.3
Mo	4	0.3
Zr	4	0.3
Mn	3	0.3
Pb*	3	0.3
B	1	0.1
Ba*	1	0.1
Ce	1	0.1
Nb	1	0.1
Ni	1	0.1
La	0.6	0.05
Cd*	0.5	0.04
Sr	0.5	0.04
Li	0.3	0.03
Nd	0.2	0.02
Ag	0.1	0.01
Hg*[a]	0.1	0.01
Rb	0.1	0.01
Y	0.1	0.01
Sb*	0.08	0.007
Se*	0.06	0.005
As*	0.03	0.003
Be*	0.01	0.001
Co*	0.01	0.001

[*] Potentially toxic metals – ACGIH TLV of <1 mg/m^3 for an 8-hour exposure (Reference 3).

[a] Determined by atomic fluorescence.

the element mercury was determined by a highly quantitative atomic fluorescence technique in order to be sure of an accurate measurement.

4.1.2 Methyl Methacrylate (MMA) Waste

The MMA waste was a medium brown liquid with a gritty sediment that tended to settle out of solution. The waste also had two liquid phases which at least partially separate on standing. It had a strong pungent odor characteristic of acrylic acid compounds. Heat content on this waste could not be determined due to its high water content. Its other physical characteristics were:

- Viscosity of 1.42 centistokes at 37°C
- Specific gravity of 1.0158 at 15°C
- LOI of 98.3 percent
- Water content of 38 percent

Elemental analyses performed showed the composition of the waste to be:

carbon — 38.2 percent
hydrogen — 9.5 percent
nitrogen — 0.06 percent
sulfur — 0.08 percent
halogens as chlorine — 0.73 percent

4.1.2.1 Organic Composition

The composition of the organic constituents of the aqueous methyl methacrylate waste burned at Systech is presented in Table 4-3. The identification and quantitation was performed by GC/MS using normalized total ion monitor response for the quantitative estimates. This method of quantification is not as accurate as calibrating instrument response for each individual waste constituent but it provides a good indicator of the relative amounts of each waste constituent present and is sufficient to meet the objective of the analysis.

The composition of the representative waste sample is considerably different than that of the survey sample from which the analytical plan was formulated (Reference 1). The basic difference is the large amount of water, 38 percent, in the representative waste. There was also a larger number of organic constituents in the representative waste. Notable among these additional constituents were a considerable amount of phenol and cresols. Their presence is intriguing but most likely due to cross contamination from the phenol waste tests. Since the run tank containing the methyl methacrylate waste had just previously been used for the phenol waste run tank, it is possible that some residual, phenol rich, sludge may have remained in the tank.

Table 4-3. Organic Composition of Methyl Methacrylate Waste Representative Sample

Compound	Estimated Levels (percent w/w)[a]
Methanol	4.9
Acetone	0.7
Methylene chloride	0.7
2-Butanone	1.1
Methyl propanoate	0.4
Methyl methacrylate	33.9
2-Ethoxy ethanol	0.4
Toluene	1.1
Xylene	0.9
2-Ethoxy ethyl acetate	0.4
Phenol	12.6
Cresols	3.4

[a] Sample contains 38 percent water and approximately 1.7 percent nonignitable solids.

The presence of dimers, trimers and possibly higher polymers from methyl methacrylate has been suggested in manufacturers literature as possibly being present in the waste. Polymerization, which can occur in reagent grades of these compounds without the addition of an inhibitor, is not believed to have any impact on the performance of the incinerator/reactor since the polymer is also readily combustible under the conditions used at Systech.

A survey analysis of the MMA representative sample of the actual waste burned at Systech was analyzed by IR and LRMS to look for species not necessarily detected in the other analyses. An IR spectrum of the MMA representative waste sample was obtained from an aliquot of the sample from which the water had been removed by evaporation at approximately 50°C. The IR indicated an aliphatic ester. Comparison of the standard IR spectra for methyl methacrylate monomer and polymers with the waste sample spectrum indicated that some polymerization had taken place. The MMA monomer had evaporated off, but its presence had already been established by GC/MS. A strong peak at 2920 cm^{-1} indicated that higher molecular weight hydrocarbons, perhaps as oils, are likely present in the waste. There were no other features in the spectra which indicated any other classes of compounds.

The LRMS data on the same residue used in the IR show that hydrocarbon oils are the major constituents of the residue after removal of water and volatiles. (The volatiles were quantified by GC and are discussed earlier.) Adipates and/or sebecates as well as some phthalate esters are present in minor amounts. The levels which these materials are present in the waste is estimated at much less than 1 percent. There is no mass spectral evidence of polymerized methyl methacrylate. The LRMS spectrum interpretation can be found in Table D-8 in the appendix.

4.1.2.2 Trace Elements

Trace elemental analysis was performed by SSMS. This analysis showed the major elements to be sodium, sulfur, and titanium. The concentrations of other elements detected down to 0.1 ppm as well as all toxic elements are presented in Table 4-4. The corresponding concentrations of these elements in the resulting combustion gas have been calculated based on average fuel and air feed conditions at Systech and are also included in the table. The SSMS data are typically accurate within 500 percent and should thus be regarded only as estimates. For this reason, and also because its volatility makes it extremely difficult to detect by SSMS, the element mercury was determined by a highly quantitative atomic fluorescence technique in order to be sure of an accurate measurement.

4.2 OPERATIONAL PROCEDURES

Detailed operating procedures, including both a test plan and a safety plan, were reviewed and approved prior to arrival of the TRW sampling team on site. Procedures and operating conditions were also recorded during the field tests. Following are brief summaries of both plans, a test-by-test commentary on events that took place in the field, and information on the disposal of the waste residues.

4.2.1 Test Procedures

Fluidized bed reactor tests were run with two wastes, phenol and methyl methacrylate, as previously described in Section 4.1. The basic procedure for each waste test was:

- Connect waste tanker and operate recirculation system
- Obtain waste sample and fresh scrubber water sample
- Verify instrumentation and sampling systems ready
- Ignite on auxiliary fuel (No. 2 oil) and stabilize temperatures
- Activate on-line analyzer system
- Initiate waste fuel combustion and observe effluent
- Stabilize flow rates and temperatures
- Extended burn duration
    - Process data acquisition
    - Combustion gas composition data acquisition

Table 4-4. Trace Metals in the MMA Waste

Element	Approximate Concentration in Waste (ppm)	Calculated Theoretical Concentration in Combustion Gas (mg/m^3)
Al	160-315	9-18
Ca	160-315	9-18
Pb*	160-315	9-18
Si	110	6.4
Mg	75	4.4
P	57	3.3
Cr*	38	2.2
Fe	38	2.2
Ba*	35	2.0
Zn	26	1.5
Cd*	21	1.2
Cu	19	1.1
Mn	10	0.6
Pt	4	0.2
Sn	4	0.2
Bi	2	0.1
K	2	0.1
Mo	2	0.1
Ni	2	0.1
Sb*	2	0.1
Sr	2	0.1
Ag	0.4	0.02
Co*	0.4	0.02
Zr	0.4	0.02
B	0.2	0.01
Rb	0.2	0.01
V*	0.2	0.01
Nb	0.1	0.006
W	0.1	0.006
As*	0.04	0.002
Hg*[a]	0.03	0.002
Be*	0.006	0.0003
Se*	0.004	0.0002

*Potentially toxic metals — ACGIH TLV of <1 mg/m^3 for an 8-hour exposure (Reference 3).

[a] Determined by atomic fluorescence.

  - Combustion zone and stack gas sampling
  - Spent scrubber liquid sampling
- Transfer to auxiliary fuel combustion
- Shutdown and secure
- Acquire sand sample from reactor bed

The test series for each waste consisted of two burn periods during which a 3-hour combustion gas sample was acquired at steady state operating conditions. A 3-hour sampling run with No. 2 oil only was also required to obtain background data.

Target test conditions for each waste were:

- Fluidizing air flow rate — 425 m^3/min
- Auxiliary fuel flow rate — 15 liters/min
- Waste flow rate — 30 to 50 liters/min
- Average bed temperature — 760^{o} to 815^{o}C

Waste flow rates were selected for each test to evaluate the effects on destruction efficiency, if any, of varying the waste/auxiliary fuel volumetric flow rate ratios between 2:1 and 3:1. Air and auxiliary fuel flow rates were held essentially constant to maintain a fluidized bed temperature between 760^{o} and 815^{o}C.

4.2.2 Safety Procedures

Safety requirements for handling and incinerating these specific wastes were established and adhered to, including the following:

- Only authorized personnel with prior approval were permitted in the test area during operations.
- Waste hookup and unloading were performed only by personnel wearing suitable protective clothing and trained in handling such materials.
- Water hose with a pistol-grip nozzle was available in the immediate area for washdown of personnel or spills.
- Visual observation of the test system was maintained at all times during operation.
- Canister gas masks and emergency oxygen resuscitation units were available in immediate area.
- Emergency agencies' telephone numbers were posted near the test area.

4.2.3 Test Commentary

Two test conditions were evaluated with both the phenol and methyl methacrylate wastes. Since auxiliary fuel was required for the combustion of each waste, a baseline test was conducted with No. 2 oil only to obtain background data. For convenience in facility scheduling, the first phenol test was performed before the background data test.

Test I – First Phenol Test

After stabilization of bed temperature at an average of 760°C with No. 2 oil, waste phenol flow was initiated. Waste flow was gradually increased until bed temperatures began to decrease below 760°C, then flow was held constant until system temperatures stabilized. Waste and fuel oil rates were checked, and the waste/auxiliary fuel volumetric flow ratio was 3.0:1. Combustion zone and stack gas sampling were then conducted at steady-state reactor operating conditions. Average temperatures were 740°C in the bed and 899°C in the freeboard volume above the bed. Combustion zone sampling was performed for 2-1/4 hours before the probe gradually became plugged with the fines from the sand bed and sample flow decreased to zero. Although a 3-hour hot zone sample was intended, the actual sample acquired was of sufficient quantity for analysis, and the test was terminated. The probe plugging instance is discussed further in Section 4.5. Calculated combustion zone residence time was 14 seconds.

Test II – Background Test

A baseline test was performed with No. 2 oil to obtain background data on combustion zone and stack gases with auxiliary fuel only. No nozzle plugging occurred, and a 3-hour combustion zone sample was obtained at steady-state operating conditions of 777°C bed and 793°C freeboard average temperatures. A 1-hour stack gas sample was also acquired during the same period. Residence time for this test and all subsequent tests was 12 seconds.

Test III – Second Phenol Test

The second test condition with waste phenols was performed at a lower waste flow rate than the first test, reducing the waste/auxiliary fuel volume flow ratio to 2.3:1. Average steady-state operating temperatures were 757°C in the bed and 813°C in the freeboard. After 1 hour of combustion zone sampling, the probe again began plugging and sample flow decreased. An air back purge through the probe did not remove the obstruction, but a water back purge cleared the probe, and the 3 hours of sampling at the hot zone was completed. Some particulate in the sample probe was lost by back purging during the run, as described in Section 4.5.

Test IV – First Methyl Methacrylate Test

Each of the methacrylate tests was performed with a watery waste, rather than the concentrated waste originally expected (see Section 4.1 for detailed explanation). The first test was conducted at a waste/auxiliary fuel volume flow ratio of 2.0:1. Average steady-state operating temperatures were 774°C in the bed and 824°C in the freeboard. A

3-hour combustion zone gas sample and a 1-hour stack sample were obtained without incident.

Test V – Second Methyl Methacrylate Test

The waste/auxiliary fuel flow ratio was increased to 2.6:1 for the second methacrylate test. Stack and combustion zone gas samples were acquired at average temperatures of 788°C in the bed and 843°C in the freeboard. The test was terminated after 2 hours and 43 minutes of hot zone sampling when bed temperatures began to increase at steady flow conditions. Since the waste tank was nearing depletion, the temperature increase was most likely due to a stratification in the waste. A recirculation system was used to mix the wastes in the tanker trailer, but mixing was apparently inefficient. As a layer of more highly concentrated waste was reached, bed temperatures increased. The auxiliary fuel oil feed rate was gradually reduced to maintain constant temperatures. It was finally turned off completely, but the bed temperatures continued to increase. Since an adequate gas sample had already been acquired, the test was terminated rather than reduce waste flow rate to compensate for the bed temperature rise.

4.2.4 Disposal of Waste Residues

The phenol waste consigned by Systech for these tests was consumed in the tests. The tank trailer was returned to the Systech facility where it was washed out with water. The washings were introduced into Systech's waste treatment plant. There was residual methyl methacrylate in the tank trailer after the testing was completed. This excess was returned to the Systech facility where it was introduced into their normal recovery and treatment process for this waste.

The scrubber waters were pumped to the municipal water treatment plant adjacent to the Systech and Black Clawson facilities. There was no disposal of the sand contained in the reactor. Additional sand was added to the existing bed to compensate for sand losses prior to and during the tests.

4.3 SAMPLING METHODS

Sampling methods used in the tests at Systech were chosen to cover three basic areas:

(1) Continuous, on-line monitoring of gas composition to determine and follow steady state conditions

(2) Collection and concentration of hot zone combustion products to identify and quantify the trace organic and inorganic species formed

(3) Collection of final emission and waste products to evaluate the environmental safety of the tests

Following is a brief summary of the methods for each of these areas. More detailed discussions can be found in the Systems Technology Analytical Plan (Reference 1). The locations of the trailer and sampling trains at the site are shown in Figures 4-1 and 4-2.

4.3.1 On-Line Gas Monitoring

Gases were drawn continuously from the hot zone through a ceramic probe and then through a heated Teflon sample line to the trailer. The gas then entered the system shown in Figure 4-3. The gas conditioner supplied a cool, dry, particulate free sample to all of the analyzers with the exception of the hydrocarbon (HC) monitor which used an untreated sample. A heated Teflon line carried the HC gas sample from a tee in the unconditioned sample line to the HC analyzer.

The monitoring instruments used are listed with their operating ranges in Table 4-5. Data was recorded on Hewlett-Packard 680M strip chart recorders. Figure 4-4 shows the instrument racks mounted in the sampling trailer. The analyzers, recorders, and manifold valves were all located in racks to provide ease of operation and accessibility.

4.3.2 Sampling of Combustion Products

The sampling train used to collect hot zone gases, vapors, and particulate is shown schematically in Figure 4-5. It consisted of a standard EPA Method 5 train with the following important modifications presented in order according to flow direction through the train.

- There was a stainless steel jacketed, water-cooled probe (shown schematically in Figure 4-6) with a quartz liner. The liner provided an inert surface for the sample gas and the cooled, stainless steel jacket cools this gas in order to quench any further reactions of the sample constituents and to yield a gas temperature compatible with train materials. Further cooling of the gas can be achieved by aspirating an air/water mixture into the space between the steel jacket and quartz liner.

- Special fittings were fabricated to allow a back purge of the probe with purified compressed air while the sampling train was not in operation. This eliminated the possibility of contamination from the relatively high amounts of organic, partial combustion products produced during start-up and shutdown of the incinerator. The back purge connection was made at the point where the dogleg from the probe liner mates with the filter housing.

- A chromel/alumel thermocouple was potted into the dogleg going from the quartz probe liner to the filter housing to check the temperature of the gas stream at that point.

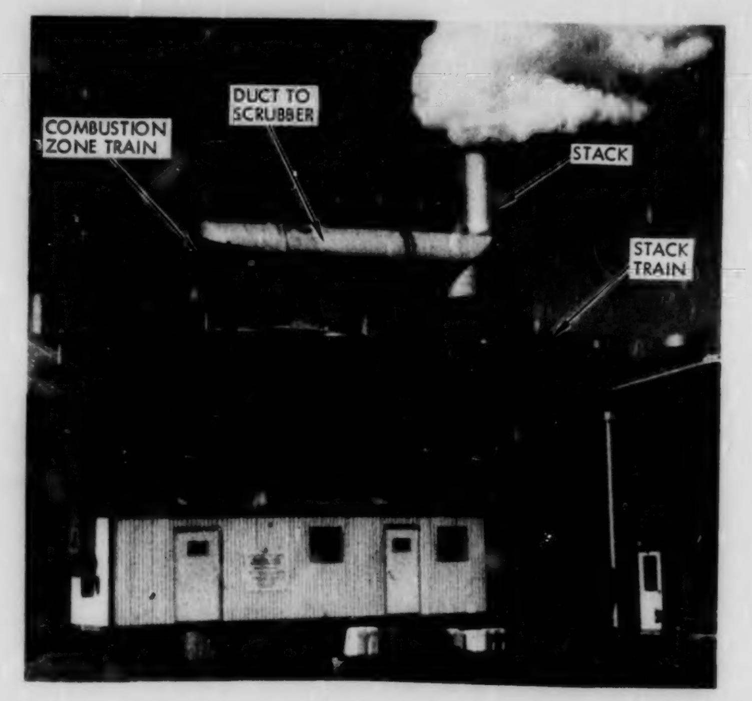

Figure 4-1. Location of Trailer and Sampling Trains at Systech

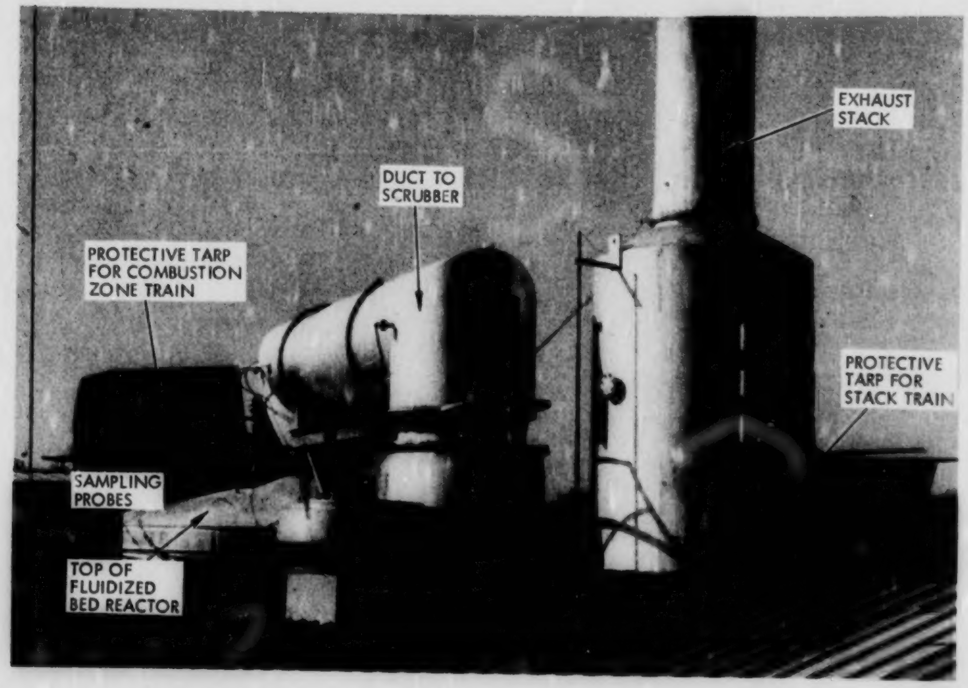
EXHAUST STACK
DUCT TO SCRUBBER
PROTECTIVE TARP FOR COMBUSTION ZONE TRAIN
PROTECTIVE TARP FOR STACK TRAIN
SAMPLING PROBES
TOP OF FLUIDIZED BED REACTOR

Figure 4-2. Closer View of Sampling Train Locations

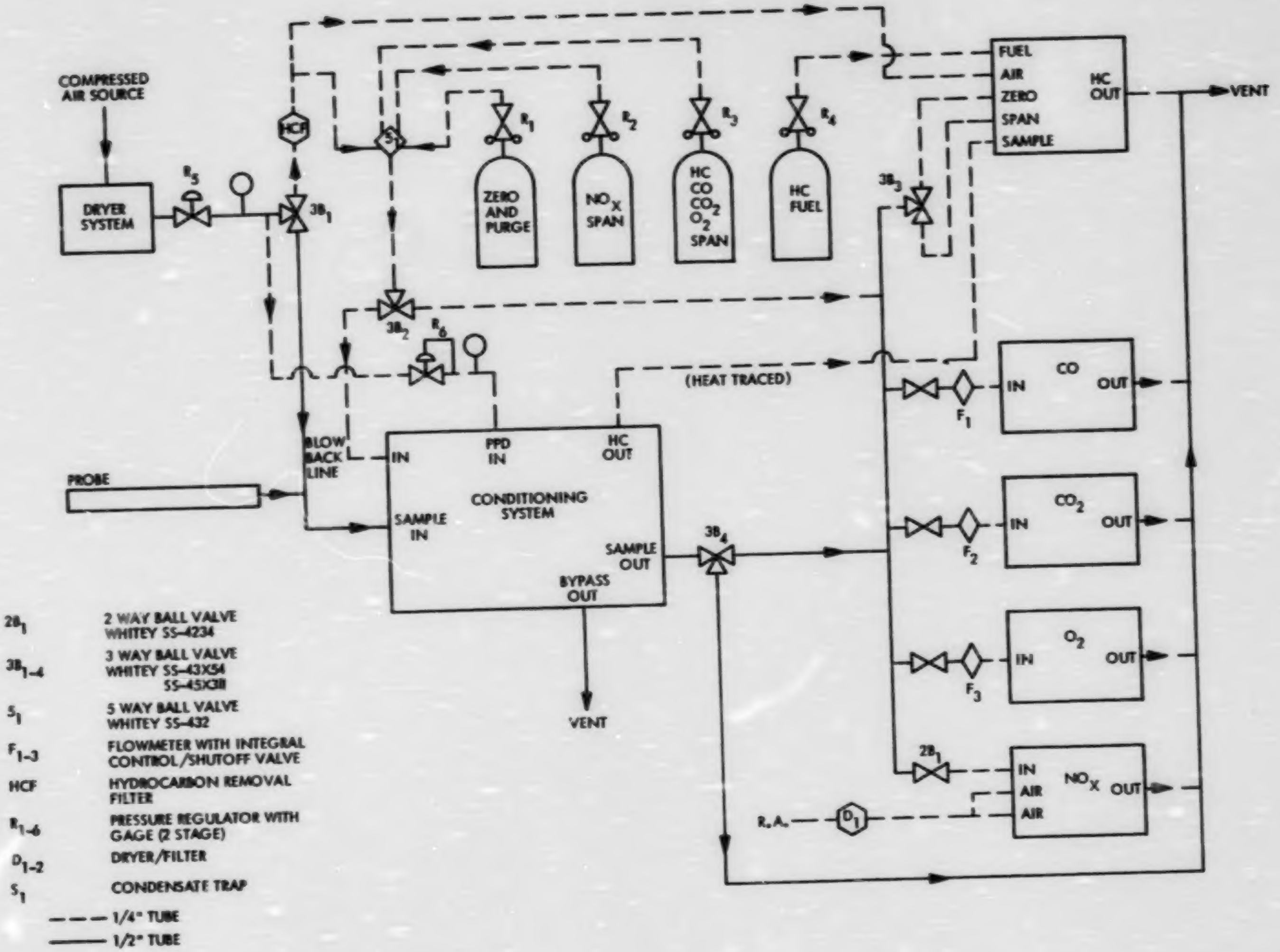

Figure 4-3. Sampling System For On-Line Instruments

Table 4-5. Description of On-Line Instruments

Species Analyzed	Manufacturer and Model	Range*
Total hydrocarbons (HC)	Beckman model 402	0.05 ppm – 10% with eight ranges
Carbon monoxide (CO)	Beckman model 865	2-200 ppm 10-100 ppm
Carbon dioxide (CO_2)	Beckman model 864	0.05 – 5% 0.02 – 20%
Oxygen (O_2)	Taylor OA 273	0.05 – 5% 0.25 – 25% 1 – 100%
Oxides of nitrogen (NO_x)	Thermo Electron model 10-A	0.05 – 10,000 ppm with eight ranges

*All of these manufacturers report an accuracy of ±1 percent of full scale for their instruments.

- An ultrahigh-purity glass fiber filter was used, Gelman Spectroquality Type A. The filters were muffled to remove organics and have extremely low background levels of inorganics. They were tared by desiccating and weighing on consecutive days to a constant weight (±0.1 mg), and were then stored and handled throughout the tests and analyses in glass petri dishes.
- A solid sorbent trap, designed to adsorb the organic constituents in the sample gas stream, is located downstream of the heated filter and upstream of the first impinger. The sorbent trap, with overall dimensions of 170 x 45 mm, contained ∿40 g of XAD-2, an Amberlite resin of the type commonly used as a chromatographic support.
- A Teflon valve was added to the glass connector between the sorbent trap and the first impinger through which glass bulbs or Tedlar bags were filled with the sample gas to be analyzed for volatile or gaseous components not collected by the sorbent traps.

This hot zone train was operated at a flow rate of approximately 30 liters/min for 3 hours during each test, thereby sampling an average of 4 to 5 cubic meters. Gas volumes were measured to 0.03 liter, with

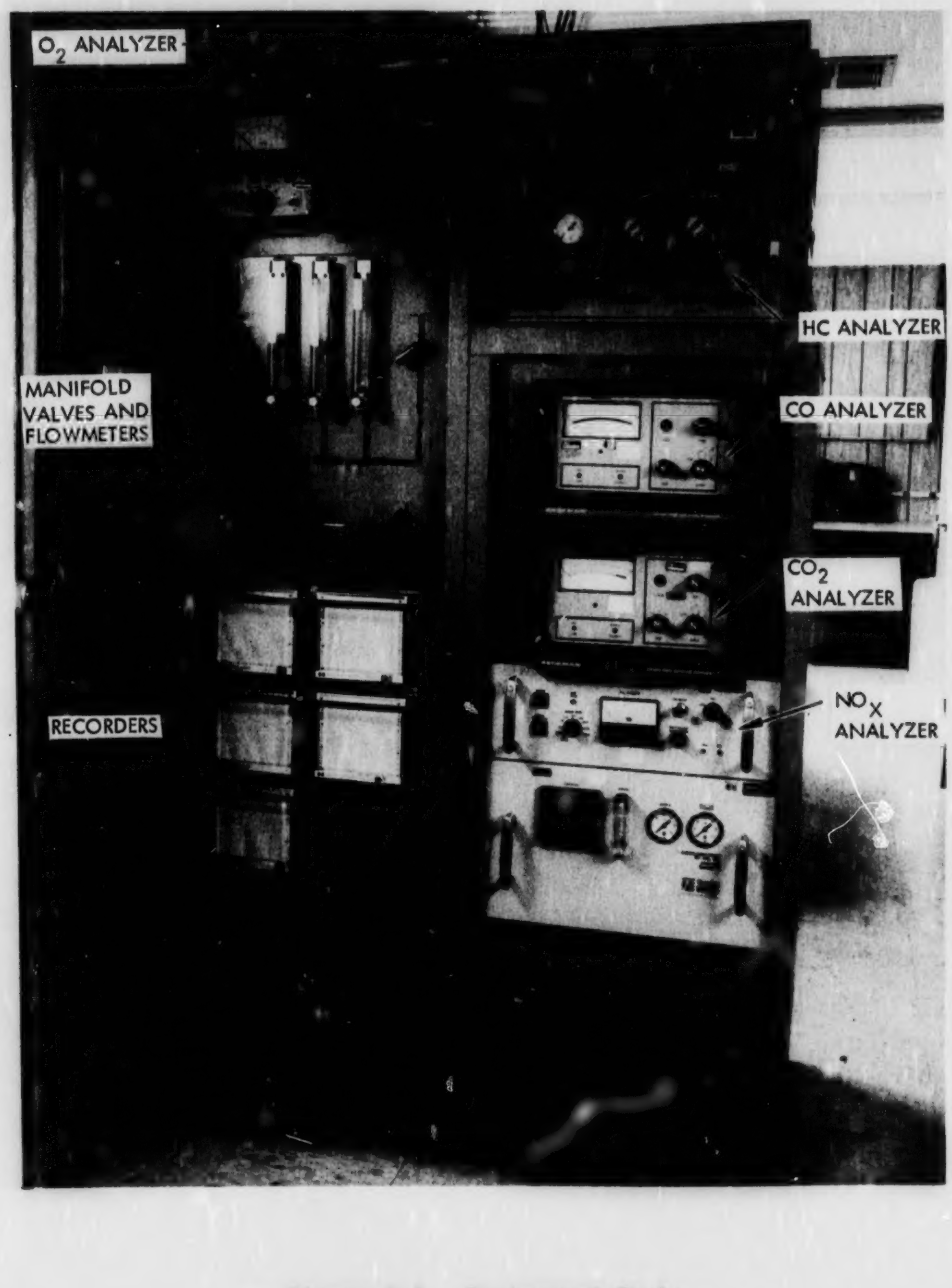

Figure 4-4. Instrument Racks

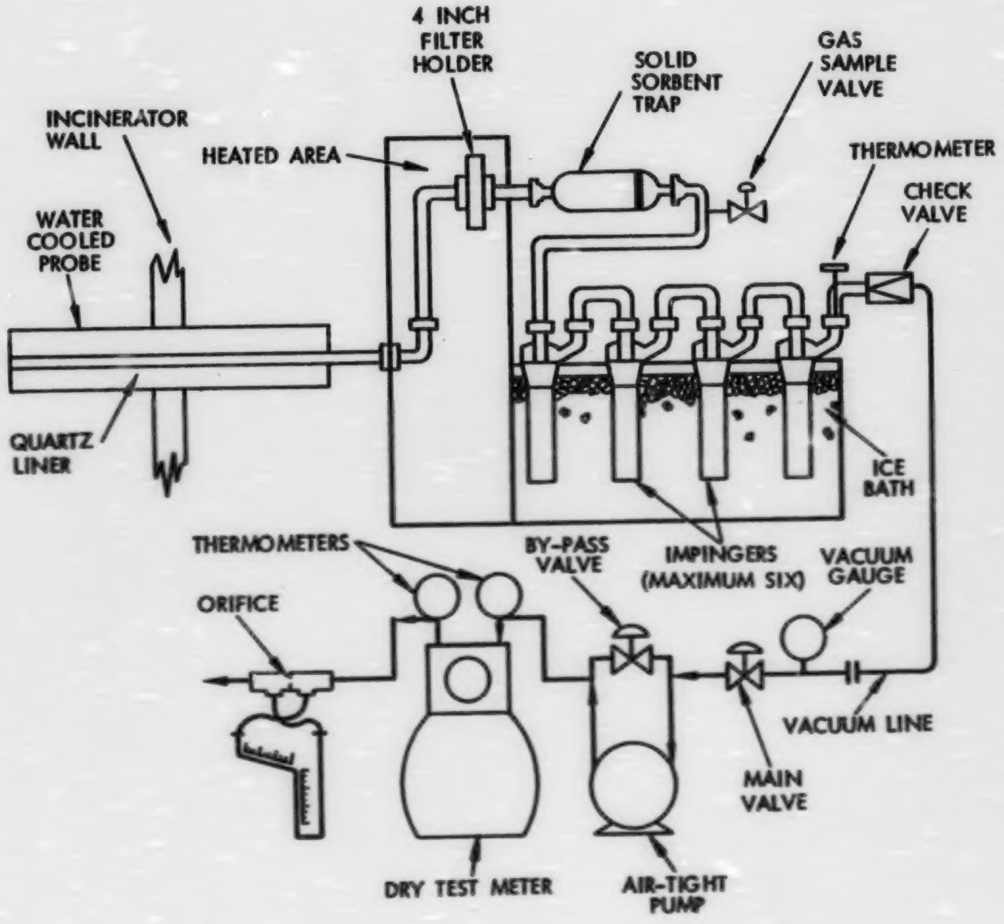

Figure 4-5. Combustion Zone Sampling Train Schematic

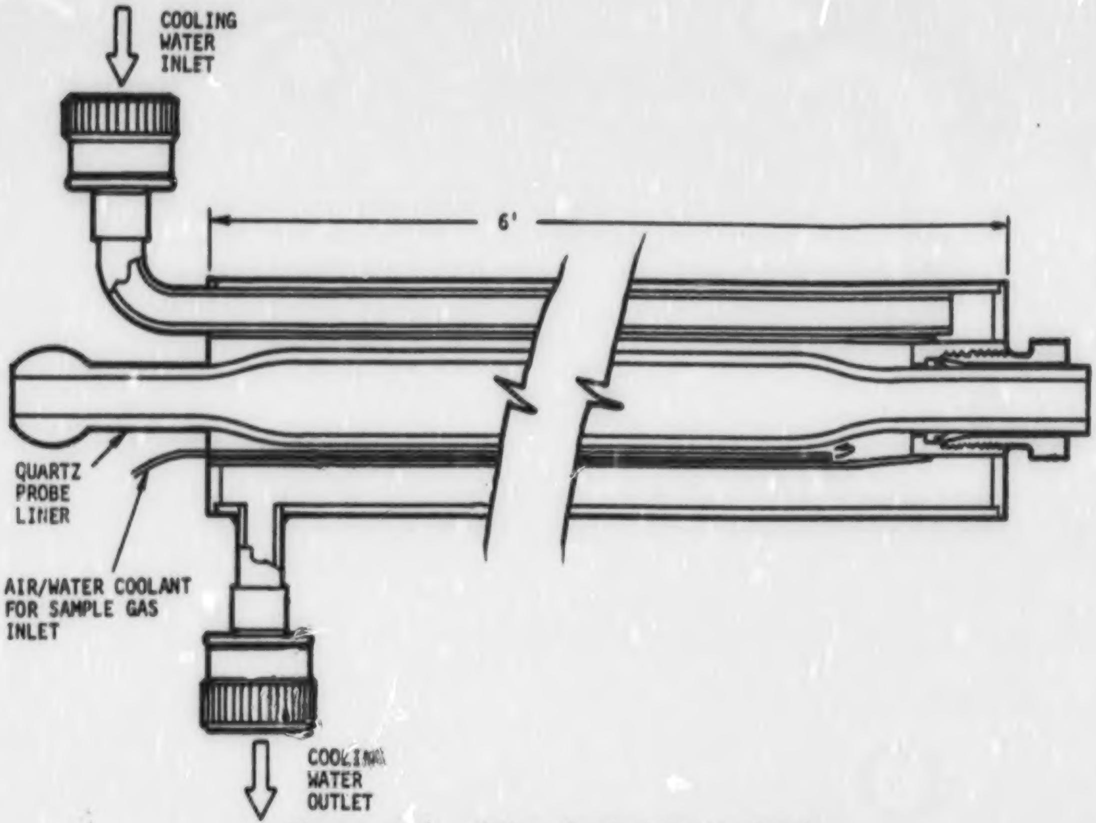

Figure 4-6. Water Cooled Probe Design

a leak rate of less than 0.6 liter/min. Operating parameters for the train and sample volume data are tabulated in Appendix B.

The following hot zone samples were obtained from each test:

- Solvent probe wash
- 10 cm diameter particulate filter
- Solid sorbent trap
- Grab gas
- Combined impinger solutions
- Acidified split of combined liquid impingers
- Spent silica gel

The location of the hot zone sampling train at the test site is shown in Figures 4-1 and 4-2.

4.3.3 Sampling Emissions and Waste Products

Samples of the stack effluent, spent scrubber water, and solid combustor residue (bed sand), were taken during and after each test to evaluate the environmental safety of the final emissions. An EPA Method 5 test was performed at the stack for particulate mass loading and composition determinations. Location of the sampling train at the test site is shown in Figure 4-2. Only one point in the 3-meter diameter stack was sampled. Selection of the sample point is discussed in Section 4.5. Sampling was carried out for 1 hour at approximately 20 liters/min. Gas volumes were measured to 0.03 liter, with a leak rate of less than 0.6 liter/min. Operating parameters for the train and sample volume data are tabulated in Appendix B.

Oxidizing agents (H_2O_2 and $(NH_4)_2S_2O_8$) were added to the impingers to aid scrubbing of trace metals. The following samples were obtained for each test from the stack sampling train:

- Aqueous probe wash
- 10-cm diameter particulate filter
- Impinger solutions
- Acidified split of impinger solutions
- Spent silica gel

Scrubber water samples were taken from a tap in the scrubber recirculation line. Prior to each test the scrubber system was filled with city water, cycled through the scrubber system and then drained. The system was then filled and circulated again before the fresh scrubber water (FSW) sample was taken. The spent scrubber water (SSW) was sampled immediately after the test was concluded. The sample was taken from the same tap with the recirculation pump still operating in order to maintain mixing and prevent sedimentation. The scrubber water samples were placed in one gallon glass jugs and were refrigerated prior to shipment to TRW.

The fluidizing sand sample was taken approximately one half hour after each test was concluded. The effect of the fluidizing air was considered adequate to have thoroughly mixed the sand during the test. A 0.7 kg representative sample was placed in an amber glass jar for storage and shipment.

4.4 ANALYSIS TECHNIQUES

Samples taken as described in Section 4.3, were analyzed for both organic and inorganic constituents. When necessary, extractions were performed first to concentrate the sample in a suitable form for analysis. Techniques used for these extractions and analyses will be briefly summarized here. For more detailed discussions, see the Systems Technology Analytical Plan (Reference 1).

4.4.1 Extractions and Sample Preparation

Both solvents and acids were used to extract organics and inorganics respectively, from the appropriate samples. These procedures and the basic sample preparation steps are listed by sample type:

- Probe Washes

  Combustion Zone

  The quartz liner had been rinsed first with pentane to remove organic matter. A water rinse was added to the procedure in order to remove the fine particulate upon which the pentane had little effect. The aqueous probe rinsings, particulate included, were extracted with pentane, first by adding the pentane probe rinsings, then with additional portions of clean pentane. This pentane extract was combined with the pentane solution from the filter extractions. The particulate was recovered, dried and weighed. The weight value was then added to the filter weight.

  Stack

  The aqueous probe rinse was evaporated to dryness and the residue weighed. This weight was added to the weight of the particulate on the filter for total mass loading calculations in accordance with EPA Method 5 procedures.

- Filters

  Combustion Zone

  The tared sample filters plus two controls were desiccated and weighed on consecutive days to a constant weight ±0.1 mg, and then extracted in a Soxhlet apparatus for 24 hours with pentane. Solvent extracts were evaporated to 10 ml for analysis. The filters were then plasma ashed and extracted with constant boiling aqua regia for two hours. This acid extract was reduced to 50 ml for analysis.

  Stack

  The tared sample filters were weighted as for the combustion zone filters, low temperature plasma ashed, and extracted with constant boiling aqua regia for two hours. The acid extracts were reduced to 50 ml for analysis.

- Solid Sorbent Traps

  Combustion Zone

  The XAD-2 resin was extracted in the Soxhlet-type apparatus shown in Figure 4-7 with pentane and methanol for 24 hours

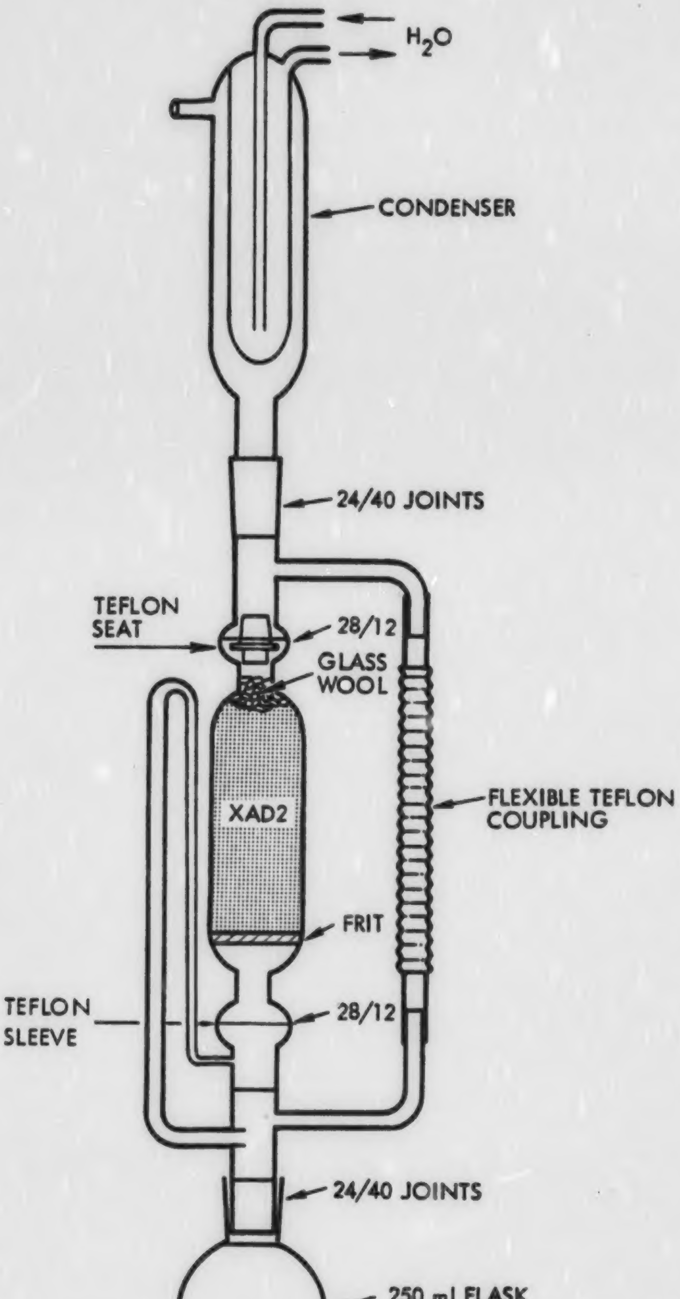

Figure 4-7. Sorbent Trap Extractor

with each solvent. These extracts were evaporated to 10 ml for analysis. Two unused traps were also extracted for background values and a blank on the solvent was also run.

Stack

No solid sorbent traps were used in the stack sampling train.

- Grab Gas

Combustion Zone

No special preparation was required.

Stack

No gas samples were taken at the stack.

- Impingers

Combustion Zone and Stack

The volume of liquid in the impingers was measured and the spent silica gel was weighed in the field after each test burn to determine the amount of water collected. The liquid impingers from the combustion zone were also combined and 150 to 300 ml aliquots acidified in the field to stabilize the metals for analysis. The stack impinger samples were also acidified. No extractions or other special preparation steps were performed on any of the impinger samples.

- Scrubber Waters

300 to 1000 milliliter aliquots of the scrubber water samples were extracted for organics according to the procedure for the separatory funnel extraction for oil and grease from water recommended by the EPA Handbook on Methods for Chemical Analyses of Water and Wastes with the substitution of pentane for Freon (National Environmental Research Center, Cincinnati, Ohio, 45268, EPA-626-/6-74-003). However, instead of evaporating the material to the dried residue, the extracts were concentrated to a 10 milliliter sample by use of a Kuderna-Danish concentrating evaporator. Aliquots of this 10-milliliter sample were then used for the survey analysis (IR and LRMS) and for gravimetric determination of residual material after evaporation at ambient conditions and immediate weighing.

- Solid Combustion Residues

Approximately 150 g portions of the sand sample from the fluidized bed were extracted in a Soxhlet apparatus for 24 hours with pentane. The solvent extracts were then evaporated to 10 ml for analysis.

4.4.2 Analytical Methods

After extraction of the samples for organic material and other preparation for inorganic material, the concentrated extracts, and aqueous solutions were analyzed by several methods which are summarized in Table 4-6. A general treatment of the sample preparation and analytical procedures is discussed below.

4.4.2.1 Organic Analyses

The concentrated solvent extracts of the filters, sorbent traps, scrubber waters, and sand bed samples were analyzed by gravimetry, IR, LRMS and GC techniques. An aliquot of each extract was evaporated at ambient conditions to remove the solvent. The residue was weighed and analyzed by IR and LRMS.

The IR and LRMS analyses yield qualitative information about the classes or types of compounds (e.g., hydrocarbons, phenols, POMs, etc.) present as well as an idea of the complexity of the concentrated sample. Knowledge of the classes of compounds present provides a measure of the toxicity, if any, of the residue. The detection limits for these analytical techniques vary somewhat with the type of compound (see Table 4-6).

The grab gas samples contained in the Tedlar® film bags were analyzed on the mass spectrometer. The bags were placed in a covered box and heated to about 70°C to ensure vaporization of any condensate. A portion of the gas sample was vacuum transferred into the inlet system of constant volume and measurable pressure. Test samples were introduced to the mass spectrometer with interspersed control samples of standard ppm butane as well as background control samples to ensure that the instrument was not slowly accumulating a "memory" in the m/e peaks of interest.

Separation and quantitation of organic compounds known to be present in the wastes and therefore possibly present in the concentrated extracts, were performed by gas chromatography with flame ionization detection (GC/FID) using the following parameters:

- Varian 1860, dual differential FIDs
- Columns: dual, 183 x 0.32 cm o.d. stainless steel, 3% SE-30 on 100/120 mesh Chromosorb WHP
- Temperatures: column, 35° to 250°C at 6°C/min, 8 minute hold at 250°C; injector, 250°C; detector, 300°C
- Flow rates: helium carrier, 30 ml/min; air, 300 ml/min; hydrogen, 30 ml/min
- Attenuation: 1 x 10^{-10} a/mv full scale

The SE-30 columns were substituted for the Chromosorb 102 columns mentioned in the Analytical Plan for Systech (Reference 1), when it was determined that they would provide a general improvement in performance.

Table 4-6. Summary of Analytical Methods

Method	Instrument Manufacturer and Model	Detectability for a Compound or Element Being Searched For
Organic Analyses		
Gravimetry	Mettler, microbalance	1 μg
Infrared Spectrophotometry (IR)	Perkin Elmer, 521	~3-5% of the sample being examined
Low Resolution Mass Spectrometry (LRMS)	Hitachi-Perkin Elmer, RMU-6 Mass Spectrometer	~10 μg (1% of a 1 mg sample)
Gas Chromatography (GC)	Varian, 1860 dual FID	
Combined Gas Chromatography/Mass Spectrometry (GC/MS)	Varian, 1860 GC and Hitachi-Perkin Elmer, RMU-6 MS	~1 μg per μl of sample
	or	
	Finnigan, 9500 GC and Finnigan, 3100D Quadrapole Mass Spectrometer	~100 ng per μl of sample
Inorganic Analyses		
Inductively Coupled Plasma Optical Emission Spectrophotometry	Applied Research Laboratories, QA-137	~0.5-2000 ppb

Table 4-6. Summary of Analytical Methods (Continued)

Method	Instrument Manufacturer and Model	Detectability for a Compound or Element Being Searched For
Atomic Absorption Spectrophotometry (AAS)	Jarrell Ash, 810	~1-0.001 ppm
Spark Source Mass Spectrophotography (SSMS)	AEI Scientific Apparatus Ltd., MS 702R	~50-100 ppb

4.4.2.2 Inorganic Analyses

Inorganic analyses were performed using atomic absorption spectrophotometry (AAS), and inductively coupled plasma optical emission spectrophotometry (ICPOES). Selected samples of the acid extractions of the stack particulate filters and the acidified splits of the impingers were surveyed for trace metals by ICPOES. The ICPOES analysis determines 32 elements, including most of the toxic elements of interest to the program, down to ppb levels with an accuracy of 100 to 200 percent. The purpose of this survey is primarily to check that the metals in these test samples are in approximately the same amounts relative to each other as they were in the waste material. Those elements which from the results either of the ICPOES survey or of the analysis of the waste material seem to be present at potentially toxic levels, were determined quantitatively by AAS. The sensitivity of this method varies from approximately 1.0 to 0.001 ppm for the elements which were determined, with an accuracy between 10 to 50 percent.

In addition to the AAS and ICPOES analyses performed on the test samples, spark source mass spectrophotography (SSMS) was used to analyze the waste materials for trace elements.

4.5 PROBLEMS ENCOUNTERED

Problems which occurred during the Systech test program are described in the following paragraphs. In spite of detailed planning and preparation for these field tests, a few incidents occurred that had not been anticipated. Corrective actions were immediately taken in each case, and testing was completed as scheduled. All required samples were obtained, and no problems were encountered in the laboratory analyses.

4.5.1 Vortex Flow in Exhaust Stack

Velocity traverses made in the exhaust stack indicated a steep gradient in velocity, with flow in the center of the stack even reversing in direction. This flow condition results from the tangential flow of gases from the scrubber duct into the vertical stack without any straightening vanes to redirect the flow. This anomaly was also observed by previous sampling teams (Reference 2) at this facility. Since standard EPA Method 5 (Reference 3) stack sampling techniques were not suitable for this turbulent flow, the decision was made to sample at the average velocity point. All stack samples were taken at this point, located 0.6 meter inward from the wall of the exhaust stack, which was 3 meters in diameter at the sampling location.

4.5.2 Combustion Zone Sample Probe Plugging

Plugging of the quartz liner of the hot zone sampling probe occurred during both of the waste phenol destruction tests. The first phenol test (Test I) was terminated after a sufficient sample had been acquired, but at less than the 3 hours intended (2-1/4 hours), because of plugging. Combustion zone sampling during the second phenol test (Test III) was performed for the full 3 hours by back purging the probe liner with water when plugging occurred. A small amount of particulate was flushed from the probe liner during this purge, affecting the total material weighed at the conclusion of the test, and must be estimated as part of the particulate loading. The probe was most likely plugged by fine sand particles from the reactor bed. The Black Clawson operators indicated that burning of watery wastes, such as the phenols, usually causes fracturing and depletion of the reactor bed sand.

4.5.3 Variation in Concentration of Methyl Methacrylate Waste

The methyl methacrylate waste received for the test program had a high percentage of water compared to the waste sample received earlier. Arrangements for supplying the waste in each case was made by Systech. When the waste to be destructed was found to be different than the original sample, the waste supplier was contacted by Systech. Systech was then informed that the watery waste was more typical of the plant waste stream. For this reason, the watery waste methacrylate was destructed during this test series using No. 2 oil as auxiliary fuel to support combustion. Samples of the waste feed were taken to undergo the same analysis procedures performed with the initial waste samples.

4.5.4 Saturation of Gastec® Tubes with Condensed Water

During the testing at Systech, it was planned to use the Gastec® tubes at the wet scrubber outlet in the same manner as they were used at the first facility. Both the Marguardt and the Systech effluent gases were saturated with water vapor but the considerably cooler ambient temperatures at Systech made condensation in the Gastec® tubes a significant problem. The indicating solids were completely saturated with condensed water and no readings could be obtained.

Pieces of copper tubing a few meters long and a glass, water-knock out trap were used at Systech in an attempt to correct the problem. However, this approach was unsuccessful and the solid contents of the tubes still became saturated. In addition the use of a condensing apparatus raises the question of whether the sought for species is being removed from the gas as a result of the condensation, thereby resulting in an erroneously low reading.

Bendix Corporation, the manufacturers of the Gastec tubes, was contacted and they also felt that the tubes will not operate reliably, if at all, when water condenses in the indicating portion of the tubes. They also agreed that removing the water by means of condensing or passing the gas stream through a drying agent will likely result in low values due to either gas solubility in the condensed water or gas absorption/reaction on the drying agent.

In future field tests, Gastec tube measurements will have to be made where the gases are dry. The best place for this is the sample by-pass output of the gas conditioner. Values measured at the by-pass outlet would indicate composition before the scrubber, and not the final effluent concentration. However, species found to be at safe levels before the scrubber can be assumed to be at safe levels in the final effluent gases.

4.5.5 Exhaust Plume Fallout

During the first phenol waste test, a lingering blue-gray haze was observed trailing the normal steam plume from the exhaust stack. This test was performed at a phenol feed rate of 50 liters/min and at a waste/auxiliary fuel ratio of 3:1. For the subsequent tests, waste feed flow rate was reduced, and plume fallout was no longer observed. Analytical results later indicated that a waste destruction efficiency of over 99.999% was achieved during the first phenol waste test even at the 50 liters/min feed rate.

5. TEST RESULTS

The test burns at Systech consisted of a background test on the auxiliary fuel (No. 2 oil), two tests of phenol waste, and two tests of methylmethacrylate (MMA) waste. The results of these tests described in the following sections include:

- Data taken in the field during the tests
- Data from analysis of the test samples in the laboratory

5.1 OPERATIONAL AND FIELD DATA SUMMARY

The data presented in this section were collected from the operation of:

- Systech fluidized bed incinerator facility
- TRW on-line gas composition monitors

All recorded data for the incinerator operating conditions were provided by Systech and are summarized in Table 5-1. Temperatures and pressures in the reactor stayed fairly consistent through each test and from one test to another. Conditions at the sampling port for the combustion zone train were closest to those reported for the reactor freeboard.

Readings from the on-line gas monitors were continuously recorded on strip charts. Resulting scans were averaged over the 2-3 hour long test runs and concentration values obtained are shown in Table 5-2. Percent excess air was calculated according to the equation in EPA Method 3 (Reference 3).

An attempt was also made to use the Gastec® tubes to detect SO_x and hydrocarbon species at the stack. However, because of the high moisture content of the stack gases and low ambient temperatures, the detection tubes became saturated with condensed water and thus accurate readings could not be obtained. The condensation problem was discussed further in Section 4.5.

5.2 ANALYTICAL DATA SUMMARY

The data obtained from analysis of all samples taken during the five test burns at Systech will be presented in this section in the following order with the organic composition discussed before the inorganic composition:

Combustion Zone

- Combustion gas

Table 5-1. Incinerator System Parameters Data Summary

Test No.	I	II	III	IV	V
Waste Tested	Phenols	-(1)	Phenols	Methyl Methacrylate	Methyl Methacrylate
Waste/Auxiliary Fuel Ratio	3.0:1(2)	-	2.3:1	2.0:1	2.6:1
Flow Rates					
Waste (liters/min)	49.9	-	33.6	29.5	36.4
Aux. fuel (liters/min)	16.4	12.1	14.8	15.0	14.0
Fluidizing Air (m^3/min)	350	435	425	425	425
Overbed Air (m^3/min)	72	105	105	105	105
Scrubber Quench Water (liters/min)	2.3	2.3	2.3	2.3	2.3
Scrubber Seal Water (liters/min)	1.6	1.6	1.6	1.6	1.6
Temperatures					
Reactor Bed TE-1 (°C)	743	782	760	774	791
Reactor Bed TE-2 (°C)	757	779	763	777	791
Reactor Bed TE-3 (°C)	721	766	749	771	782
Reactor Bed Controller (°C)	735	779	754	771	788
Reactor Freeboard (°C)	899	793	813	824	843
Reactor Duct North End (°F)	888	768	796	796	841
Scrubber Inlet (°C)	85	76	80	80	82
Scrubber Outlet (°C)	92	82	85	85	91
Pressures					
Waste Feed Pump (kilopascals)	270	-	190	140	190
Windbox (cm H_2O)	152	157	168	168	163
Bed Differential (cm H_2O)	81	79	86	81	81
Freeboard (cm H_2O)	8.9	10.7	17.8	15.7	14.7
Exhaust Oxygen (percent)	9.6(3)	14.8	17.7	14.5	14.1
Calculated Residence Time (sec)	14	12	12	12	12

(1) Background test with auxiliary fuel (No. 2 oil) only

(2) Volumetric flow ratio — liters per minute waste/liters per minute auxiliary fuel

(3) Oxygen content of exhaust gases in stack as measured by Black Clawson personnel

Table 5-2. Gas Composition Data Summary

Test No.	O_2 (percent)	CO_2 (percent)	CO (ppm)	NO_x (ppm)	N_2 (percent)	HC (ppm)[a]	EA[b] (percent)
I	10.7	9.4	6-7	56	79.9	5-20	103
II	15.4	5.9	5	10	78.7	10-50	286
III	12.6	7.6	8-26	41-51	79.8	0-33	149
IV	13.4	7.4	8-10	--[c]	79.2	0-40	178
V	11.6	8.0	10-20	--[c]	80.4	0-10	121

[a] As methane

[b] Excess air

[c] Instrument was down due to a broken power supply

Final Emissions

- Stack gas
- Scrubber water
- Solid Residue (bed sand)

Methods and techniques for the preparation and analysis of the test samples can be found in Section 4.4.

5.2.1 Combustion Products

Samples of the combustion products were taken from the head space above the fluidized bed reactor with the sampling train described in Section 4.3.2. These samples were then separated into their organic and inorganic constituents and analyzed by appropriate techniques. Analysis of the combustion products is aimed mainly at identifying and quantifying any unburned waste material or hazardous partial combustion products. The production of potentially toxic levels of trace metals from burning these wastes is also examined. Where quantified species are calculated back to mg/m^3 in the sample gas stream, the gas volume data used is summarized in Appendix B.

5.2.1.1 Organic Composition

The organic analyses were divided into: (1) quantitative determination of uncombusted known constituents from the waste material or other specific compounds that could be expected to be present, and (2) qualitative surveys to identify unexpected compounds.

Quantitation for Specific Compounds

Specific compounds such as phenol, cresols, and methyl methacrylate monomer were analyzed by gas chromatography with flame ionization detection (GC/FID). Samples which yielded quantities at or above the level of interest were also analyzed by combined gas chromatography/mass spectrometry (GC/MS) to identify the compounds present. The level of interest for this program is defined as 0.1 mg/m^3 of sample gas, the threshold level of nearly all the most toxic species as defined by OSHA and other health and safety organizations. Detection limits for many of the quantitative techniques used extend down to $\mu g/m^3$ levels. However, specific analyses to identify compounds below the level of interest were not routinely performed.

Results of Gas Chromatographic Analyses

This section presents the results of the analysis for the specific constituents of the wastes which were identified as being present in the survey and representative waste samples. Gas chromatography with flame ionization detectors (FID) were employed. The details of this analytical procedure can be found in Section 4.4. The instrument parameters were established so that all the compounds listed in Tables 4-1 and 4-3 would be well separated and could be detected if present at or below the criterion level of 0.1 $\mu g/m^3$. The instrument was calibrated, i.e., instrument response was measured, with known amounts of pure phenol and methyl methacrylate monomer (MMA) which are the principal organic constituents of the wastes.

At the instrument sensitivity settings used for all the samples, the minimum detectable quantities were:

- phenol: 0.003 microgram per microliter of concentrated extract ($\mu g/\mu l$)
- MMA: 0.02 microgram per microliter of concentracted extract ($\mu g/\mu l$)

These minimum detectable quantities when related to the average combustion zone sample gas volume of about 4.5 m^3 are 0.007 and 0.04 mg/m^3 for phenol and MMA, respectively. These values change somewhat depending on sample volume size (Table B-2).

The results of the GC analysis for the specific organic waste constituents plus possible unexpected compounds are given in Table 5-3. The table shows that none of the compounds found in the waste were detected above the limits set for phenol and MMA which are described earlier. Table 5-3 thus has been completed with "ND" (not detected) and the appropriate minimum

Table 5-3. Results of Gas Chromatographic Analyses of Combustion Gas Samples

Sample	MMA Waste, Constituents,[(a)] mg/m^3 as MMA	Phenol/Waste Constituents,[(a)] mg/m^3 as Phenol
SY-I-CG-PF & PW	--	ND (<0.01)
SY-II-CG-PF & PW	ND (<0.04)	ND (<0.01)
SY-III-CG-PF & PW	--	ND (<0.01)
SY-IV-CG-PF & PW	ND (<0.04)	--
SY-V-CG-PF & PW	ND (<0.05)	--
SY-I-CG-ST-P	--	ND (<0.01)
SY-I-CG-ST-M	--	ND (<0.01)
SY-II-CG-ST-P	ND (<0.08)	ND (<0.01)
SY-II-CG-ST-M	ND (<0.08)	ND (<0.01)
SY-III-CG-ST-P	--	ND (<0.01)
SY-III-CG-ST-M	--	ND (<0.01)
SY-IV-CG-ST-P	ND (<0.07)	--
SY-IV-CG-ST-M	ND (<0.07)	--
SY-V-CG-ST-P	(Lost)	(Lost)
SY-V-CG-ST-M	ND (<0.09)	--

ND:	Not detected
PF & PW:	Combined organic extracts from the particulate filter and probe washings
ST-P:	Sorbent Trap; pentane extract
ST-M:	Sorbent Trap; methanol extract

(a) See Tables 4-1 and 4-3 for list of waste constituents detectable quantity. The minimum detectable quantities vary somewhat depending on the size of the original gas sample (Table B-2). The units for all the hot zone samples are milligrams of species per cubic meter of sampled gas, water vapor included.

Analytical Efficiency

Table 5-4 reports the results of the analyses of several control samples used to determine recoveries or analysis efficiencies. An unused sorbent trap was doped with phenol and designated SY-CG-ST-C3. Similarly, a MMA doped trap was designated SY-CG-ST-C4. They were extracted, concentrated, and analyzed using the same procedures for the sample traps. In addition, city water was doped with known amounts of phenol and MMA, extracted, concentrated, and analyzed just as the scrubber water samples. From the sorbent trap, the recovery of phenol is excellent, and the recovery of MMA is adequate. The table shows that the first extraction with pentane recovered the bulk of the dopants. From the tap water, the recovery of phenol is poor, and the recovery of MMA is excellent. It should be noted that the extraction and analysis procedures used for the Systech samples have been standardized for all test samples from all facilities in this program. Thus these procedures cannot be expected to be optimum for each species of interest. The recovery factors given in Table 5-4 have been applied to the appropriate Systech samples shown in Table 5-3, especially as they relate to the minimum detectable levels of phenol and MMA in the various sample forms studied. It was noted that in all cases the minimum detectable levels are below 0.1 mg/m^3 an agreed upon level below which analyses are curtailed.

Table 5-4. Results of Gas Chromatographic Analyses of Sorbent Trap Extraction Controls

Sample Name	mg Taken		mg Found		Percent Recovery	
	MMA	Phenol	MMA	Phenol	MMA	Phenol
Phenol Doped Trap; Pentane Extract	-	6.2	-	6.1	-	98
Phenol Doped Trap; Methanol Extract	-		-	<0.03	-	<0.5
MMA Doped Trap; Pentane Extract	13.1	-	6.5	-	50	-
MMA Doped Trap and Methanol Extract		-	<0.2	-	<1.5	-

Qualitative Surveys

Samples were surveyed by gravimetric, infrared spectrometry (IR), and low resolution mass spectrometry (LRMS) techniques. Since the qualitative results correlate more to sample type than to waste burn, the data are discussed in the following order:

- Combined particulate filter and probe wash extracts
- Sorbent trap extracts
- Grab gas samples.

Combined Probe Wash and Particulate Filter Extracts

The types of organic material found in this survey are typical of those compounds found in most of the other organic residues obtained in the survey analyses from these tests. Hydrocarbon oils, phthalic acid esters, silicone oils (or greases), and an antioxidant were found. The amounts at which these materials were found are presented in Table 5-5. The values have been corrected for those obtained from blanks and controls which were considerably lower.

Further separation and identification of these compounds were not carried out because of the relative nontoxic nature of the classes of compounds represented. Additional details of the survey analyses on these samples can be found in Appendix D.

Table 5-5. Summary of Survey Analysis on the Combined Probe Wash and Particulate Filter Extracts

Test No.	Volume of Sampled Gas[a] (m^3) 1 atm and 21°C	Amount of Material Found as Residue[b] (mg)	Concentration in Sample Gas (mg/m^3)
I	3.29	7.76	2.4
II	5.13	6.20	1.2
III	4.45	1.11	0.2
IV	5.57	7.85	1.4
V	4.22	5.32	1.3

[a] Includes water vapor

[b] Corrected for blank extraction thimbles and solvent

Sorbent Traps

The amounts of material extracted from the sorbent traps and found as a residue after mild evaporation are presented in Table 5-6. The amounts have been corrected for the unused, control sorbent trap extracts. On the average, the sample trap extracts had four times the residue as the control trap extracts. The types of material found in the trap extracts by IR and LRMS analyses were essentially the same for all samples.

The compounds found in the extracts from the sorbent traps consisted primarily of hydrocarbons and phthalic acid esters. Fatty acids and a squalene type compound(s) were also present at lesser levels. Traces of silicones were present in some of the samples. Details of the IR and LRMS spectra interpretation are described in Appendix D.

The fact that the residues from the sample traps average four times greater than the residues from the control traps tends to indicate that the traps did indeed collect these materials while in the hot zone train. However, the general makeup of the residues is essentially the same in both sample and control trap extracts and this raises some doubt as to the main source(s) of these compounds. No work was performed to examine this situation in greater detail because of the general, nontoxic nature of the residues found.

Grab Gas Samples

The contents of the Tedlar® gas sampling bags were analyzed by introducing a portion of the gas into the mass spectrometer and measuring its pressure at constant volume. Spectral evidence of the common, expected components of both air and the combustion gases, such as N_2, O_2, H_2O, CO_2, H_2, CO, and AR, were seen. In addition, evidence of ppm levels of hydrocarbons were also seen as evidenced by peaks at 41, 43, 55, and 57 AMU. No evidence of any other organics was detected and this includes the waste constituents (e.g., phenol and MMA).

A 14 ppm butane in nitrogen standard was used to determine instrument response to hydrocarbons at the same pressures and volumes used for the samples. Using the height of the 43 AMU peak for calibration, the hydrocarbon levels in the grab gas samples were measured. The results, corrected for instrument background, are listed in Table 5-7. The results show 2 to 4 ppm as butane, C_4H_{10}. When these values are multiplied by four to obtain a hydrocarbon value as methane, CH_4, the resulting range of 8 to 16 ppm is in fair agreement with the on-line hydrocarbon analyzer data (Table 5-2).

Table 5-6. Summary of Survey Analysis on Sorbent Trap Extracts

Test No.	Material Extracted by Pentane (mg)[a]	Material Extracted by Methanol (mg)[a]	Total Extractables (mg)[a]	Volume of Sample Gas (m^3)	Concentration of Extractables in Sample Gas (mg/m^3)
I	8.0	9.3	17.3	3.29	5.2
II	8.5	26.0	34.5	5.13	6.7
III	5.4	25.0	30.4	4.45	6.8
IV	7.7	26.5	34.2	5.57	6.1
V	Sample Lost	4.1	Not Available	4.22	Not Available

[a] Corrected for control sorbent trap extract weights.

Table 5-7. Approximate Hydrocarbon Content in Grab Gas Samples by LRMS

Test No.	Hydrocarbon Level (ppm as butane)
I	2
II	3
II*	4
III	2
IV	3
V	3

*Redundant sample was taken at the hydrocarbon analyzer bypass outlet.

5.2.1.2 Inorganic Characterization

Inorganic elemental concentrations were determined by analysis of the particulate filters and aqueous impinger samples. Figure 5-1 shows a photograph of the particulate filters obtained from sampling the combustion gases from Tests I through V, in order going from left to right and top to bottom. Trace metals on the particulate filters were put into solution by acid digestion of the filters. Quantitative analysis for selected elements were then performed by atomic absorption spectrometry (AAS). The elements to be analyzed were selected by the following criteria:

(1) Potentially toxic (e.g., Pb, Cd, Sb, and Hg)

(2) Present at significant levels as determined by the: (a) survey analysis of the wastes (Section 4.1), and/or survey analysis of the stack filter acid digests (Section 5.2.2.1).

Using these criteria, seven elements were selected for quantitative analysis by atomic absorption spectrometry (AAS). Four potentially toxic elements (Ba, Cd, Cr, and Pb) were found at relatively high levels by the ICPOES survey of the stack filter digests. The other three elements (Sb, V, and Zn) analyzed were chosen on the basis of the waste analysis data. Both the filter digests and the impingers from the combustion zone sampling train were analyzed. Data from the filters are presented in Table 5-8, along with the stack filter data for comparison. None of the seven elements

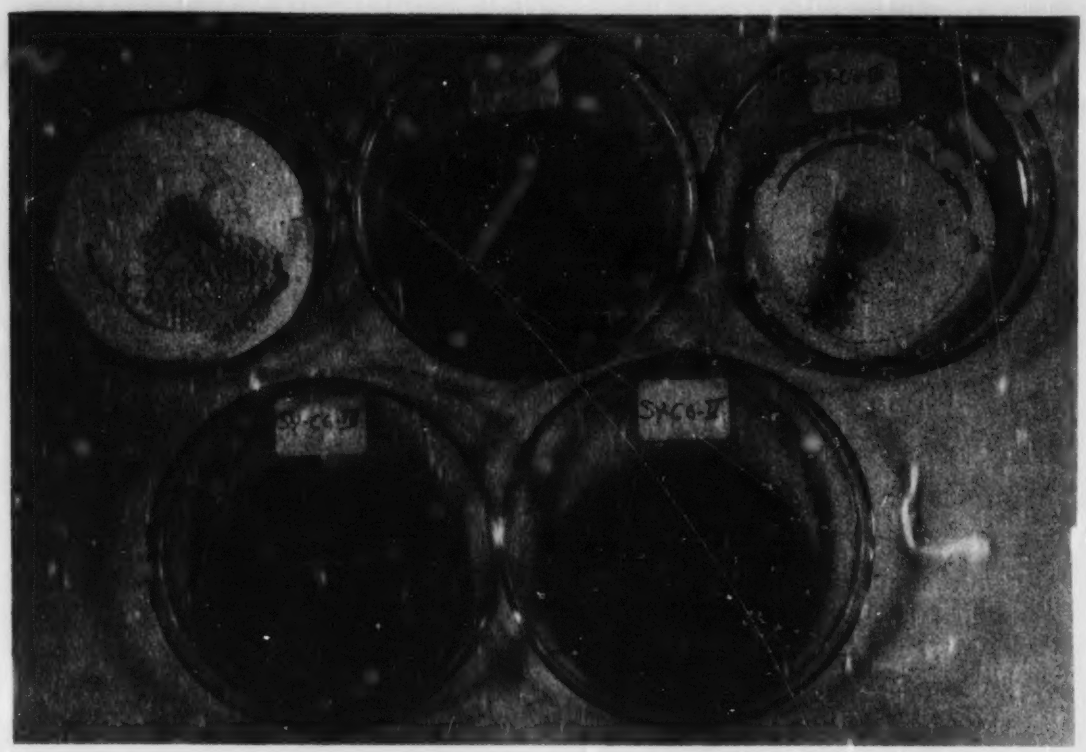

Figure 5-1. Filters from Combustion Zone Gas Sampling Train

analyzed were detected in the impinger samples. The calculated detectable limits in the combustion gas stream for these elements were:

Sb - 0.02 mg/m^3	Cr - 0.003 mg/m^3
V - 0.03 mg/m^3	Pb - 0.007 mg/m^3
Zn - 0.0007 mg/m^3	Ba - 0.03 mg/m^3
Cd - 0.001 mg/m^3	

5.2.2 Final Emissions

Emissions from the Systech fluidized bed process were sampled and analyzed to evaluate the environmental safety of the waste burns. All of the final process effluents were sampled; these were stack gas, scrubber water, and solid residue (bed sand).

Table 5-8. Trace Metals on Particulate Filters by AAS

Test No.	Sampling Train	Element Concentration in Gas Stream (mg/m^3)						
		Ba[1]	Cd	Cr	Pb	Sb	V	Zn
I	Combustion Zone	≤0.14[2]	0.029	0.068	1.16	0.029	<0.003[3]	0.36
	Stack	≤0.07	0.062	0.065	0.87	0.022	<0.004	0.24
II	Combustion Zone	≤0.27	0.009	0.10	0.13	≤0.001	<0.002	0.24
	Stack	≤0.26	0.007	0.042	0.086	≤0.021	<0.007	≤0.23
III	Combustion Zone	≤0.04	0.039	0.12	1.03	0.021	<0.002	0.25
	Stack	≤0.93	0.026	0.093	0.44	≤0.024	<0.008	0.17
IV	Combustion Zone	≤0.08	0.035	0.13	0.85	0.031	<0.002	0.32
	Stack	≤0.55	0.029	0.082	0.55	≤0.014	<0.005	0.12
V	Combustion Zone	≤0.60	0.67	0.26	4.74	0.058	<0.002	0.66
	Stack	≤0.40	0.16	0.18	2.21	≤0.012	<0.004	0.072

[1] Barium had very high and erratic background levels in the filter material.

[2] "≤", a less than or equal to sign indicates those elements which were detected but not significantly above background levels.

[3] "<", a less than sign indicates the detection limit for elements which were not detected.

5.2.2.1 Stack Gas

Stack effluents were sampled during the tests with a standard EPA Method 5 train. The samples obtained were analyzed to determine particulate loading in the effluent gas and elemental composition of the particulate. Figure 5-2 shows the particulate filters obtained from sampling the stack gas from Tests I through V, in order going from left to right and top to bottom. The Test I filter stuck to the filter housing gasket and subsequently was torn while being removed.

Particulate loading was determined by adding the weight gain on the filters to the weight of residue in the probe washes. This total was then divided by the dry sample gas volume and the loading values obtained are listed in Table 5-9.

After weighing, the filters were acid digested and selected samples were surveyed for trace metals by inductively coupled argon plasma optical emission spectroscopy (ICPOES). The results of this survey are shown in Table 5-10. Of the 32 elements that are determined by the ICPOES analysis, eleven were not detected in the filter digest samples. These eleven elements with their lower detection limits are listed in Table 5-11, along with a calculation of the average detectable limit for each of these elements in the flue gas.

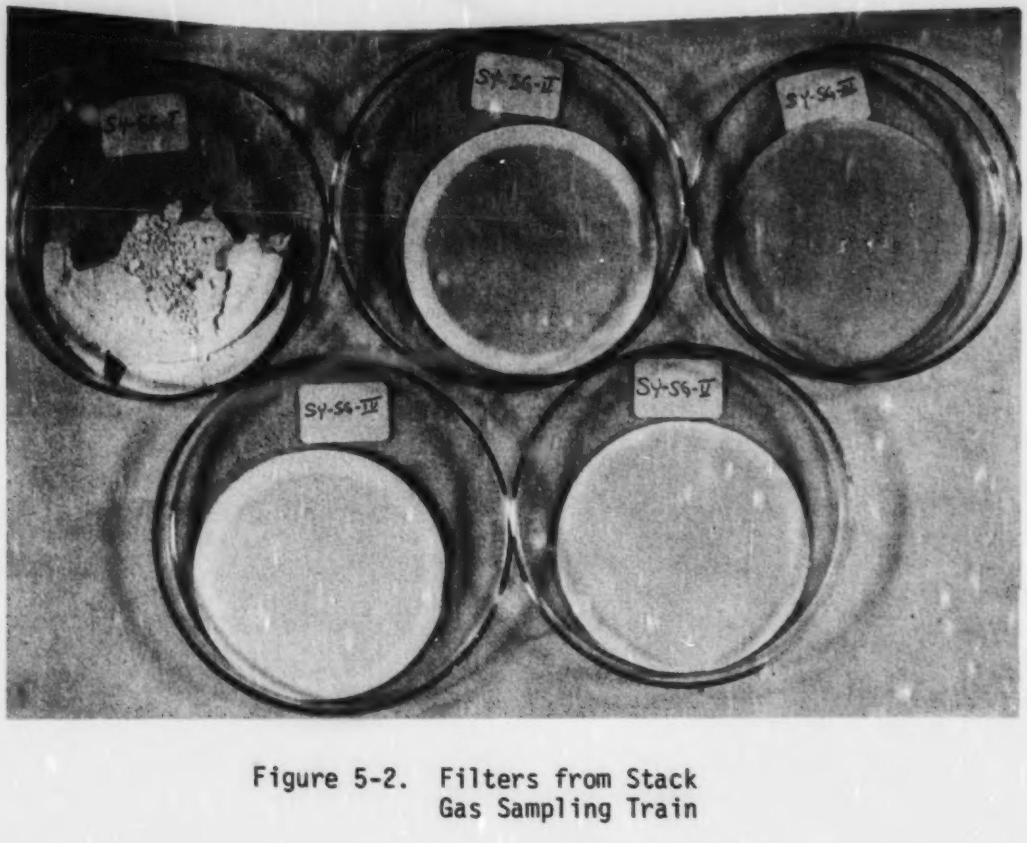

Figure 5-2. Filters from Stack Gas Sampling Train

Table 5-9. Particulate Loading in the Effluent Gas

Test	Weight on Filter (mg)	Weight in Probe Wash (mg)	Total Weight (mg)	Sample Gas Volume, Dry (m^3)	Particulate Loading	
					mg/m^3	Grains/scf
I — Phenol	2,184	47	2,231	1.56	1,430	0.62
II — Background	691	5	696	0.98	710	0.31
III — Phenol	1,084	14	1,098	0.86	1,280	0.56
IV — MMA	822	16	838	1.34	630	0.27
V — MMA	909	19	928	1.65	560	0.25

Table 5-10. Survey for Trace Metals in the Stack Filter Digests by ICPOES

Element	Concentration in Stack Gas (mg/m^3)		
	Test II (Background)	Test III (Phenol)	Test V (MMA)
Al	≤0.55[a]	≤0.72	≤0.83
Ba	≤0.44	≤0.90	≤0.44
B	≤0.83	≤1.5	≤0.38
Ca	0.55	1.01	1.6
Cd	0.007	0.016	0.15
Cr	0.036	0.061	0.13
Cu	0.035	0.47	0.38
Fe	0.15	4.5	0.56
Pb	0.082	0.40	2.3
Mg	≤0.36	≤0.31	≤0.53
Mn	0.004	0.015	0.013
Ni	0.004	0.012	ND (<0.0002)
P	0.075	0.31	0.68
K	ND (<0.012)	3.1	2.4
Si	≤0.28	≤0.09	≤0.07
Ag	0.004	0.001	0.013
Na	2.7	89.	23.
Sr	≤0.015	≤0.017	≤0.018
Ti	0.082	0.048	0.088
V	0.0005	0.0015	0.0008
Zn	≤0.15	≤0.28	≤0.22

[a] "≤", a less than or equal to sign indicates those elements which were detected but not significantly above background levels.

Table 5-11. Limits of Detection for Elements Undetected by ICPOES

Element	ICPOES Detection Limit (ppb)	Average[a] Detectable Limit in Flue Gas (mg/m^3)
Au	5	0.0001
As	40	0.001
Be	1	0.00003
Co	16	0.0004
Eu	15	0.0004
Mo	11	0.0003
Se	60	0.002
Te	65	0.002
Sn	50	0.001
W	90	0.002
U	80	0.002

[a] Based on an average wet sample gas volume of 2.0 m^3

The results of this survey indicate four elements (i.e., cadmium, chromium, lead, and barium) are present at potentially toxic levels. To be sure of an accurate measurement of the levels of these and certain other toxic metals which the waste analysis indicated might be present at levels of interest, a quantitative determination by AAS was performed on seven elements. Data obtained from the AAS analyses on the stack filter digests is summarized along with data from the combustion zone filter digests in Table 5-8. The AAS data confirms the ICPOES survey in that there were relatively high levels of certain elements in the effluent gas.

Trace metals in the form of very fine particulate or vapor can pass through the filter. Thus to be sure of a quantitative measurement of total metal emissions, both ICPOES and AAS analyses were also performed on the impinger samples from the stack sampling train. The first liquid impinger samples from selected tests were surveyed for inorganics by ICPOES and the results are shown in Table 5-12. Only eleven elements were detected in the samples, thus most of the data in this table are detection limits for the undetected elements. The AAS analysis was performed on both the first impinger and the combined second and third impinger samples from all five

Table 5-12. Survey for Trace Metals in Stack First Liquid Impinger Samples by ICPOES

Element	Concentration in Stack Gas (mg/m^3)		
	Test II (Background)	Test III (Phenol)	Test V (MMA)
Al	<0.008[1]	<0.008	<0.005
As	<0.01	<0.01	<0.006
Ba	<0.08	<0.08	<0.05
Be	<0.0002	<0.0002	<0.0001
B	0.22	0.090	0.035
Ca	0.027	0.030	0.010
Cd	<0.003	<0.003	<0.002
Cr	<0.002	<0.002	<0.001
Co	<0.004	<0.004	<0.002
Cu	0.001	0.002	0.0004
Eu	<0.004	<0.004	<0.002
Fe	0.002	0.006	0.002
Au	<0.001	<0.001	<0.0007
Pb	<0.02	<0.02	<0.01
Mg	<0.0001	<0.0001	<0.00004
Mn	<0.0002	<0.0002	<0.0001
Mo	<0.003	<0.003	<0.002
Ni	<0.003	<0.003	<0.002
P	<0.12	<0.12	<0.07
K	8.7	10.3	3.2
Se	<0.015	<0.015	<0.008
Si	1.2	0.49	1.2
Ag	0.005	0.005	<0.00004
Na	<0.15	0.49	<0.08
Sr	<0.0002	<0.0002	<0.0001
Te	<0.02	<0.02	<0.009
Sn	<0.012	<0.012	<0.007

[1] "<", less than values indicate elements which were not detected

Table 5-12. Survey for Trace Metals in Stack First Liquid Impinger Samples by ICPOES (Continued)

Element	Concentration in Stack Gas (mg/m^3)		
	Test II (Background)	Test III (Phenol)	Test V (MMA)
Ti	0.004	0.004	0.003
W	<0.02	<0.02	<0.01
U	<0.02	<0.02	<0.01
V	0.001	0.001	<0.0001
Zn	<0.0005	0.005	<0.0003

tests. Although oxidizing reagents had been added to the impingers to enhance inorganic recoveries, none of the seven elements analyzed by AAS were detected above the reagent solution backgrounds. The calculated detection limits in mg/m^3 of flue gas for these elements were:

Sb - 0.04
V - 0.06
Zn - 0.001
Cd - 0.003
Cr - 0.006
Pb - 0.01
Ba - 0.06

The results from the impinger analysis indicate that the emitted inorganics were in a sufficiently large particulate form to be collected on the particulate filter.

5.2.2.2 Scrubber Water

The recirculated scrubber water was sampled before and after each test to obtain fresh scrubber water (FSW) and spent scrubber water (SSW) samples, respectively. Aliquots of these samples were both solvent extracted for analysis of organics and acidified to stabilize inorganics for analysis. Comparison of the analytical results for the FSW and SSW samples yields an estimate of how much, if any, hazardous species were added to the scrubber water during each test.

The FSW samples obtained contained visible suspended solids, which raised the possibility of cross-contamination between tests. It was also observed during the tests that the scrubber could not be flushed out and cleaned reliably. Thus, the analyses of FSW samples have been treated and reported as separate data and have not been subtracted from SSW results.

Organic Composition

As with other samples for analysis of organics, the scrubber water extracts were quantitatively analyzed for specific compounds and qualitatively surveyed for overall composition.

Quantitative Results

The results of the analysis of scrubber water extracts for specific waste constituents are presented in Table 5-13. None of the compounds found in the wastes, and listed in Tables 4-1 and 4-3, was found in any of the fresh or spent scrubber water extracts. The lower limits of detection are shown as the numbers accompanying the "ND" (not detected) designation. The levels are reported as phenol and MMA since these compounds were used to calibrate and measure instrument response. However it is stressed that analysis parameters were designed to separate and detect all the waste constituents as a minimum.

Table 5-13. Results of Scrubber Water Extract Analyses by GC

Test and Sample Identification	MMA Waste Constituents, mg/liter as MMA	Phenol Waste Constituents, mg/liter as Phenol
I — FSW	--	ND[a] (<5)
SSW	--	ND (<0.4)
II — FSW	ND (<0.6)	ND (<1)
SSW	b	b
III — FSW	--	ND (<1)
SSW	--	ND (<0.4)
IV — FSW	ND (<0.6)	--
SSW	ND (<0.2)	--
V — FSW	ND (<0.6)	--
SSW	ND (<0.2)	--

[a] ND = not detected

[b] SY-II Scrubber water sample was accidentally destroyed by sample bottle breakage at the Systech facility

Qualitative Survey Data

Aliquots of the solvent extracts were evaporated at ambient conditions. The residue obtained from this step was then weighed and analyzed by IR and LRMS techniques. The concentration of extractable species in the scrubber waters, as calculated from the extract residue weights is presented in Table 5-14. The data from the IR and LRMS analyses indicate that hydrocarbon based oils and phthalic acid esters are the major components of the residue. These materials are commonly used as lubricants and also as plasticisers in polymeric materials. A compound believed to be azeleic acid (nonane dioic acid) is also present at lesser levels. It is not surprising that these materials are present in scrubber liquids since the several pumps and valves that the water flows through in the facility must be lubricated.

The IR and LRMS spectra were also searched for any evidence of the constituents found in the representative wastes. No evidence of any of these species was found. Further details on the data interpretation can be found in Appendix D.

Table 5-14. Summary of Survey Analysis of Scrubber Water Extracts

Test and Sample Identification	Volume of Water Extracted (liters)	Weight of Residue in Extract (mg)	Concentration in Scrubber Sample (mg/liter)
I — FSW	0.065	1.1	17
SSW	0.903	0.9	1
II — FSW	0.345	1.8	5
SSW	--[a]	--	--
III — FSW	0.337	0.6	2
SSW	0.905	1.8	2
IV — FSW	0.351	2.7	8
SSW	0.905	0.4	< 1
V — FSW	0.348	1.6	5
SSW	0.902	1.3	1
Control Sample[b]	0.922	2.4	3

[a] Sample was lost

[b] Water with known amounts of phenol and methyl methacrylate monomer added

Inorganic Characterization

The acidified aliquots of the scrubber water samples were analyzed by AAS for seven elements including the four (i.e., Ba, Cd, Cr, and Pb) found to predominate in the filter digest samples. The results of this analysis are summarized in Table 5-15. No values are reported for the SSW sample from run I because an acidified split was not made in the field and thus a reliable sample was not available.

The data show no significant changes in trace metal concentrations and no clear trends. For Tests II and III, the FSW values are higher overall than the SSW and for Tests IV and V, the opposite is true. No conclusions can be made from this result since the flow of these trace metals through the scrubber is a dynamic process. While operating, some water in the scrubber is bled off to compensate for condensation of water in the combustion gases. Thus trace metals found in the fresh scrubber water could increase or decrease depending on water input/output rates.

5.2.2.3 Solid Residue (Bed Sand)

The bed sand is not, strictly speaking, an effluent of the Systech process. The sand charge remains in the fluidized bed with fresh make-up sand being added periodically. The objective of analyzing the sand samples that were taken at the end of each test, was to determine whether any residual hazardous materials were present which would effect disposal methods for the sand *if* it had to be disposed of. However, there is little likelihood that disposal of the sand would actually occur in practice.

Organic Composition

Portions of the sand samples were extracted in a Soxhlet apparatus with pentane. The resulting extracts were then analyzed by the quantitative and qualitative methods described previously in Section 5.2.1.1.

Quantitative Data

The results of the GC analysis for the compounds identified in the wastes and searched for in the sand residue extracts are presented in Table 5-16. The results are reported in milligrams per kilogram of sand, which is the same as ppm on a weight to weight basis. None of the compounds known to be in the phenol or MMA wastes were found in any of the sand residues above the detection limits shown in the table. Phenol and MMA monomer standards were used to determine instrument response.

Qualitative Survey Data

Evaporated aliquots of the solvent extracts were weighed and the gravimetric results are shown in Table 5-17. Milligram quantities of residues were found in the extracts. The control samples for the sand extractions did not yield enough of a residue to be weighable. Thus, no background corrections were needed. The IR data indicated only hydrocarbon oils or greases and lesser amounts of ester compounds. The LRMS data confirmed the IR results but in addition found traces of di-tert-butyl-methyl

Table 5-15. Trace Elements in Scrubber Waters by AAS (ppm)

Test No.	Ba		Cd		Cr		Pb		Sb		V		Zn	
	FSW	SSW	FSW	SSW	FSW	SSW	FSW	SSW	FSW	SSW	FSW	SSW	FSW	SSW
I	--	0.38	--	0.04	--	0.23	--	2.7	--	ND[1]	--	ND[1]	--	0.69
II	1.0	0.57	0.07	0.02	0.24	0.24	1.4	0.25	ND	ND	ND	ND	3.8	0.54
III	0.55	0.28	0.06	0.02	0.29	0.03	1.1	0.50	ND	ND	ND	ND	3.4	0.19
IV	0.52	0.56	0.01	0.03	0.03	0.17	0.25	0.45	ND	ND	ND	ND	0.45	0.79
V	0.55	0.81	0.03	0.33	0.06	0.08	0.55	1.8	ND	ND	ND	ND	1.2	0.35

[1] ND — not detected, detection limits for Sb and V are 0.5 and 0.2 ppm, respectively.

FSW — fresh scrubber water

SSW — spent scrubber water

Table 5-16. Results of Sand Extract Analysis by GC

Test No.	MMA Waste Constituents, mg/kg as MMA	Phenol Waste Constituents, mg/kg as Phenol
I	--	ND (<0.2)
II	ND (<1)	ND (<0.2)
III	--	ND (<0.2)
IV	ND (<1)	--
V	ND (<1)	--

[a] ND: not detected

Table 5-17. Summary of Survey Analysis of Sand Extracts

Test No.	Amount of Sand Extracted (kg)	Amount of Residue in Extracts (mg)	Concentration of Extractables (mg/kg)
I	0.158	8.0	51
II	0.154	7.2	47
III	0.154	5.4	35
IV	0.161	3.3	20
V	0.161	8.3	52

phenol (an antioxidant also known as BHT) and methyl abietate. Also seen in the SY-I and SY-IV samples was a trace of an incompletely identified chlorinated aromatic with a molecular weight believed to be 228. Its source is not known. Constituents of the waste materials were specifically searched for and were not detected in any of the samples. Further details of this survey work can be found in Appendix D.

Inorganic Characterization

The bed sand samples were not analyzed for their inorganic constituents for several reasons. First, since the bed sand is not recharged between runs and municipal waste was burned between TRW's tests, any residues associated with the sand could not be related to contributions from the phenol or methyl methacrylate wastes. Second, it is impossible to analyze for inorganics on the sand without analyzing to some degree the sand itself, which again would have no relationship to contributions from the wastes burned.

6. WASTE INCINERATION COST

Individual economic analyses were performed to determine the costs of incinerating, on an industrial basis, the two high water content waste materials tested at the Systems Technology Corporation incinerator at Franklin, Ohio. The economic analyses were divided into capital investment and annual operating costs. For each disposal facility, equipment prices, fuel consumption, and manpower requirements estimates for the Dorr-Oliver fluidized bed reactor-Venturi scrubber system were based on data obtained from Systems Technology Corporation. The costs of other portions of the disposal facilities and associated labor were estimated using the method of Happel ("Chemical Process Economics," second edition, John Happel and Donald G. Jordan, 1974), data from Guthrie ("Capital Cost Estimating," Chemical Engineering, March 24, 1969), and standard engineering reference methods. Equipment costs were adjusted to January 1976 prices using the Marshall & Swift Index. Land prices are not included in the two disposal plant cost estimates. Transportation costs were included for the methyl methacrylate waste disposal economic analysis, which is premised upon a central facility at Franklin, Ohio incinerating waste materials from the methyl methacrylate plants within 240 kilometer rail shipping distance. Transportation costs were not included for the phenol waste water disposal economic analysis, since the incinerator was assumed to be located at the refinery generating the waste to be disposed.

6.1 CAPITAL INVESTMENT

The capital investment for the facility to incinerate 13.2 million liters per year of aqueous methyl methacrylate manufacturing wastes shown in Table 6-1 is based upon a design concept which employs a 7.6 meter freeboard diameter Dorr-Oliver fluidized bed reactor, equipped with Venturi scrubber and auxiliary equipment. The facility costs include a methyl methacrylate waste storage tank (60-hour capacity), fixed rate waste feed pump, fuel oil storage tank (5-day capacity), auxiliary air compressor (for fuel gun insertion and removal), ash-water slurry bleed pump, and ash-water slurry settling tank (5-hour retention capacity). A sludge pump for solids removal from the settling tank, an emergency overflow sump (18925 liter capacity) for the scrubber, and twin emergency sump pumps complete the purchased equipment list. It was assumed that a waste to fuel ratio of 2.3 represented average fuel consumption for proper operation of the incinerator.

The size of the facility was based upon three-shift, 5-day per week, 52 weeks per year operation, to dispose of the 13.2 million liters of waste estimated available from plants in the Franklin, Ohio shipping area. The methyl methacrylate waste incineration plant has a nominal thermal capacity of 15 million kcal per hour; the actual thermal load, based on fuel values for the 2200 LPH of waste and 924 LPH of No. 2 fuel oil, is 70 percent of nominal thermal capacity.

The total capital investment for the methyl methacrylate waste incineration facility is estimated at $5,984,200. It should be noted that the facility would incinerate annually 11,250 metric tons of water only 1,250

Table 6-1. Capital Investment
13.2 Million Liter/Year* Methyl Methacrylate Waste Incineration Plant

Equipment	Size	Estimated Costs Equipment**	Labor
1-Dorr-Oliver reactor, Venturi scrubber, and auxiliary equipment	7.6 m free board diam.	$1,250,000	
1-Waste storage tank	13,250 liters	15,700	
1-Waste pump	2250 lph @ 400 kilopascals	800	
1-Ash-water slurry bleed pump	100 lpm	900	
1-Ash-water slurry settling tank	38,000 liters	7,400	
1-Sludge pump	200 lpm	1,000	
1-No. 2 fuel oil storage tank	100,000 liters	9,100	
1-Air compressor	2.8 scmm @ 345 kilopascals	5,300	
1-Emergency overflow sump	18,925 liters	500	
2-Sump pumps	1000 lpm	3,000	
		$1,293,700	$129,000
Instruments (10% of equipment)		129,400	19,400
(Key Accounts)		$1,423,100	$148,400
Insulation (10% of key accounts)		142,300	213,500
Piping (45% of key accounts)		640,400	640,400
Foundations (4% of key accounts)		56,900	85,400
Buildings (4% of key accounts		56,900	39,800
Structures (4% of key accounts)		56,900	11,400
Fire Protection (0.75% of key accounts)		10,700	69,600
Electrical (4.5% of key accounts)		64,000	96,000
Painting & Cleanup (0.75% of key accounts)		10,700	69,600
Equipment & Labor	$3,836,000	$2,461,900	$1,374,100
Overheads (30% of Equipment & Labor)	1,150,800		
Total Erected Cost	$4,986,800		
Engineering Fee (10% of Erected Cost)	498,700		
Contingency Fee (10% of Erected Cost)	498,700		
Total Capital Investment	$5,984,200		

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*90% (W/W) Water; 10% (W/W) Organic Liquids

**F.O.B. Cost

metric tons of liquid organic materials (almost completely insoluble in water). If the organic liquids phase of the methyl methacrylate waste were separated by centrifugation at the source plants, the capital investment for incineration of the resultant 1,420,000 liters of organic materials (equivalent to 28 days of full scale incinerator operation) could be prorated downwards, on a basis proportional to the fraction of overall operating time. This would require that the subject fluidized bed incinerator be employed for the majority of the year on wastes other than the methyl methacrylate organic liquid phase material. An additional capital outlay would be required at the waste source plants, for the facility to separate the phases by centrifugation and to remove residual organic materials from the centrifugate water phase (by techniques such as a combination of activated carbon adsorption and ozonization) to produce an acceptable industrial outfall. The total capital outlay for this alternative treatment and incineration technology would probably be slightly over $1,000,000.

The capital investment shown in Table 6-2 for the facility required to incinerate 23.8 million liters (26,300 metric tons) per year of phenol waste water is based on the fluidized bed incinerator system required at a refinery site to burn a 1:2.3 fuel oil: waste (volume) ratio, for a waste feed rate of 72,000 liters per day. The fluidized bed reactor required is 7.6 meter freeboard diameter - the size used at Franklin, Ohio. The facility design concept includes the Venturi scrubber and auxiliary equipment, a phenol waste water agitated storage tank (approximately one week storage capacity), fixed rate waste feed pump, fuel oil storage tank (1 day storage capacity), auxiliary air compressor (for fuel gun insertion and removal), ash-water slurry bleed pump, and ash-water slurry settling tank with 5-hour retention capacity. The design differs only slightly from that of the facility for incinerating methyl methacrylate waste. The remainder of the phenol waste water facility includes a sludge pump for solids removal from the settling tank, an emergency overflow sump (18,925 liter capacity) for the scrubber and twin emergency sump pumps.

The estimated capital investment for the phenol waste water incineration plant is $6,075,200, not including land cost.

6.2 ANNUAL OPERATING COSTS

The annual operating costs consist of labor, fuel, other utility, solid waste disposal and freight costs (where applicable) plus cost of capital, equipment depreciation, maintenance, taxes and insurance. The labor costs have been calculated on the number of personnel assigned to operate the system at the rates given by Systems Technology Corporation for Franklin, Ohio. Costs for supervision, supplies and payroll-related expense have been included, at rates prevalent in the chemical industry.

The utility costs include those for electricity and water consumption Annual electricity usage was calculated based on the motor horsepower requirements for the equipment sizes and capacities shown in Tables 6-1 and 6-2. Water consumption data was taken from the data given on the Dorr-Oliver process control diagram for the fluidized incinerator system. The amount of No. 2 fuel oil consumed was based on actual test data for the two wastes at the Franklin, Ohio site.

Table 6-2. Capital Investment
23.8 Million Liter/Year Phenol Waste Water Incineration Plant

Equipment	Size	Estimated Costs	
		Equipment*	Labor
1-Dorr-Oliver reactor, Venturi scrubber, and auxiliary equipment	7.6 m free board diam.	$1,250,000	
1-Waste storage tank, agitated, carbon steel	568,000 liters	38,000	
1-Waste pump	3200 lph @ 400 kilopascals	800	
1-Ash-water slurry bleed pump	100 lpm	900	
1-Ash-water slurry settling tank	38,000 liters	7,400	
1-Sludge pump	200 lpm	1,000	
1-No. 2 fuel oil storage tank	32,000 liters	6,700	
1-Air Compressor	2.8 scmm @ 345 kilopascals	5,300	
1-Emergency overflow sump	18,925 liters	500	
2-Sump pumps	1000 lpm	3,000	
		$1,313,600	$131,000
Instruments (10% of equipment)		131,400	19,700
(Key Accounts)		$1,445,000	150,700
Insulation (10% of key accounts)		144,500	216,800
Piping (45% of key accounts)		650,300	650,300
Foundations (4% of key accounts)		57,800	86,700
Buildings (4% of key accounts)		57,800	40,500
Structures (4% of key accounts)		57,800	11,600
Fire Protection (0.75% of key accounts)		10,800	70,200
Electrical (4.5% of key accounts)		65,000	97,500
Painting & Cleanup (0.75% of key accounts)		10,800	70,200
Equipment & Labor	$3,894,300	$2,499,800	$1,394,500
Overheads (30% of Equipment & Labor)	1,168,300		
Total Erected Cost	$5,062,600		
Engineering Fee (10% of Erected Cost)	506,300		
Contingency (10% of Erected Cost)	506,300		
Total Capital Investment	$6,075,200		

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*F.O.B. Cost

The annual operating costs for the incineration of 13.2 million liters of methyl methacrylate waste at a central facility are summarized in Table 6-3. The estimated annual operating expense for the plant based on 15 shift per week operating is $3,193,400, or $255.08 per metric ton. If the alternative treatment and incineration technology cited in Section 6.1 is employed, the reduction in plant investment-associated annual costs (depreciation, cost of capital, maintenance and taxes and insurance) would be over $1,700,000 with an additional reduction of over $800,000 based on zero fuel oil consumption and reduced freight cost. Order of magnitude cost-per-ton estimate for the alternative technology is $50.00.

The annual operating costs for the plant to incinerate 23.8 million liters of phenol containing waste water are summarized in Table 6-4. The estimated annual expense based on 330 day per year, three shift per day operation is $3,268,600 or $124.24 per metric ton.

The cost of capital shown is based on the assumption that private debt financing is used for each facility.

Table 6-3. Annual Operating Cost
13.2 Million Liter/Year Methyl Methacrylate Waste Incineration Plant

Item		Cost - $/Year
Depreciation (15% of plant investment)		$ 897,600
Cost of Capital (10% of plant investment)		598,400
Maintenance (8% of plant investment)		478,700
Utilities		523,200
Electric power [400 KW (24)(260) + 20 KW (24)(105)] $0.15	= $38,200	
Water 568 lpm (260)(1440) @ $0.066/1000 liter	= 14,000	
Fuel Oil, No. 2 36,230 bbl @ $13.00/bbl	= 471,000	
Solid Waste Disposal @ $6.50/ton for 9,350 metric tons		60,800
Freight 150 mi. @ $1.42/cwt 12,500 metric tons @ $31.30/metric ton		391,900
Labor		123,100
Chief Operator 1 x 24 x 260 x $6.60	= 72,400	
Operator Helper 1 x 24 x 260 x $5.00		
Supervision (15% of Operating Labor)	= 10,900	
Supplies (20% of Operating Labor)	= 14,500	
Payroll Related Expense (35% of Operating Labor)	= 25,300	
Taxes & Insurance (2% of plant investment)		119,700
	Total	$3,193,400
Cost per metric ton of methyl methacrylate waste @ 12,500 metric tons/year		$255.08

Table 6-4. Annual Operating Cost
23.8 Million Liter/Year Phenol Waste Water Incineration Plant

Item			Cost - $/Year.
Depreciation	(15% of plant investment)		$ 911,300
Cost of Capital	(10% of plant investment)		607,500
Maintenance	(8% of plant investment)		486,000
Utilities			908,700*
Electric power	[400 KW (24)(330) + 20 KW (24)(35)] $.015	= $47,800	
Water	568 lpm (330)(1440) @ $0.066/1000 liter	= 17,800	
Fuel Oil, No. 2	64,850 bbl @ $13.00/bbl.	= 843,100*	
Solid Waste Disposal	@ $6.50/metric ton for 11,900 metric tons		77,300
Labor			156,300
Chief Operator	1 x 24 x 330 x $6.60 }	= 91,900	
Operator Helper	1 x 24 x 330 x $5.00		
Supervision	(15% of Operating Labor	= 13,800	
Supplies	(20% of Operating Labor)	= 18,400	
Payroll Related Expense	(35% of Operating Labor)	= 32,200	
Taxes & Insurance	(2% of plant investment)		121,500
		Total	$3,268,600*
Cost per metric ton of phenol waste water @ 26,300 metric tons/year			$ 124.24

*In the event that other refinery wastes can be used as fuel, utility and total cost per year will decrease to $65,600 and $2,425,500 respectively; cost per metric ton of phenol waste water would then be $92.18.

7. REFERENCES

1. TRW Document #27003-6002-RU-00, "Analytical Plan for Facility No. 3. Tests to be Conducted at Systems Technology", by J. F. Clausen and D. R. Moore.

2. "Fluidized Bed and Scrubber Emissions, City of Franklin Solid Waste and Fiber Recovery Plant, Franklin, Ohio", Air Pollution Control Division, Environmental Sciences, Inc., Feb. 28, 1972.

3. American Conference of Governmental Industrial Hygienists, Threshold Limit Values, "National Safety News", October 1974.

4. Environmental Protection Agency, Standards of Performance for New Stationary Sources., Federal Register, Vol. 36, No. 247, Dec. 1971

APPENDIX A

ASSESSMENT OF ENVIRONMENTAL IMPACT OF DESTRUCTING CHEMICAL WASTES
AT
SYSTECH WASTE TREATMENT CENTER
BAXTER ROAD AT ROUTE 73
FRANKLIN, OHIO 45005

The Systech Waste Treatment Center in Franklin, Ohio, is adjacent to the Franklin Solid Waste and Fiber Recovery Plant operated by Black Clawson. Systems Technology Corporation has an exclusive contract with Black Clawson for the destruction of liquid wastes in the fluidized bed incinerator. Destruction of the following wastes will be evaluated using this incinerator:

(1) Waste phenols — 16,000 gallons (90% water)

(2) Methyl methacrylate — 3,500 gallons (concentrated)

The South-West Air Pollution Control Office, Cincinnati, Ohio, has been notified of the schedule for destruction testing of these specific wastes. The operating permit issued to the Franklin Solid Waste Recycling Plant by the State of Ohio EPA includes permission for Systech to incinerate liquid industrial wastes at this facility.

Manufactured by Dorr-Oliver, this incinerator has a capacity of up to 360 gallons per hour of high heat content liquids (over 10,000 Btu/lb) and up to 2,000 gallons per hour of liquids with a heat content of 3,000 Btu/lb. The fluidized bed system is equipped with a high energy venturi scrubber. Scrubber water is sent to the Miami Conservancy District Wastewater Treatment Plant (adjacent to the incinerator) for processing. After scrubbing exhaust gases are emitted into the atmosphere through a stack approximately 60 feet above ground level at a temperature of 180° to 190°F. Solid residue (ash) is disposed of on-site in an approved landfill.

The incinerator facility is located in the Franklin Environmental Complex, which also includes the Systech Waste Treatment Center and the Miami Conservancy District Waste Water Treatment Plant. The surrounding area includes industrial, commerical, agricultural, and residential developments. Adjacent industries include Logan Long Paper Products, a producer of roofing felt. A gasoline service station is also located nearby. The nearest residences are located approximately 250 yards east of the facility across Holes Creek (a small tributary of the Miami River) and are dispersed among small farms. Prevailing winds are from the southwest at usual velocities up to 10 miles per hour. Local vegetation includes trees, brush, weeds, and farm crops. Birds and rabbits are the most apparent wildlife in the area.

Vehicular traffic includes about 30 trucks per day hauling municipal waste to the Solid Waste and Fiber Recovery Plant (the fluidized bed incinerator also processes an average of 35 tons per day of municipal waste). Delivery of the liquid wastes for this test program has a negligible effect on overall traffic at the facility. Operation of the incinerator is only slightly noisy even within the building, and only a white steam plume can be seen from surrounding areas. The incineration facility normally operates 8 hours per day for a 4 day week, and employs eight persons.

The prevention of any detrimental environmental impacts from the following aspects of the operation are expected to result from proper control and testing: (1) storage and handling of wastes prior to destruction, (2) emissions occurring during tests, and (3) disposal of liquid and solid residue remaining after combustion. The most significant potential hazard would result from contact with waste liquid and/or fumes during a spill. The "Fire Protection Guide on Hazardous Materials," published by the National Fire Protection Association describes these wastes as follows:

Phenol (pure crystals)*	Toxic, causes severe burns, lethal amounts may be absorbed through skin or inhaled.
Methyl methacrylate	Slight irritant to eyes, skin, and respiratory tract.

Storage and Handling

Liquid wastes will be received by tank truck and transferred to storage tanks by Systech personnel trained in handling these materials. Availability and operation of safety equipment will be verified prior to any waste transfer operation. Safety equipment includes: protective clothing, fire extinguisher, oxygen mask, stretcher, and washroom facilities. Leaks and any spills will be washed down with water. All rinse or wash down liquids will be incinerated in the same manner as test wastes.

Incineration Tests

Operation temperature and residence time of the fluidized bed incinerator should provide essentially complete combustion of the wastes, resulting in harmless exhaust emissions. On-line monitoring of gases from the combustion zone will be utilized as an indication of combustion efficiency.

The venturi scrubber is expected to remove trace amounts of HCl generated by the combustion process. Emissions of SO_x should be limited since sulfur was found to be a minor waste constituent. In addition, the Black Clawson scrubber should be effective in removing particulate from the exhaust stream. Analysis of the two wastes indicated the presence of some trace metals. Of the two wastes, phenol manufacturing waste presents the worst case condition anticipated during the test burn program. Calculations for the predicted emissions levels (before scrubbing) were made to assess potential environmental problems. The results of these calculations are as follows:

Phenol Waste	
SO_2	141 ppm
HCl	9 ppm
Zn	0.03 ppm
Cr	3 ppm

---

*Waste phenols will contain 90% water.

These levels are expected to be reduced via effective scrubbing; therefore, no serious environmental problem is anticipated. As a precaution, however, stack emissions (downstream of the scrubber) will be checked for hazardous gaseous species using Gastec® analyzers for specific gases and vapors. Particulate matter will be collected using a standard EPA Method 5 sampling train.

Disposal of Residues

Residue material from the incineration process will consist of scrubber water and ash. Liquid residue from the scrubber will be analyzed by both Black Clawson and the Miami Conservancy District Wastewater Treatment Plant personnel before discharge to the on-site water treatment plant. Solid residues (ash) will also be tested by the Miami Conservancy District personnel prior to on-site landfill. Wastes remaining in the storage/run tanks and wash down liquids from any spills will be incinerated at the conclusion of the test program.

APPENDIX B

SAMPLE TRAIN OPERATION AND SAMPLE VOLUME DATA

For each test burn, data were collected on the operation of the two sampling trains. This information is presented in Table B-1. The gas velocity and stack pressure at the combustion zone (reactor freeboard) were both theoretically calculated since no pitot tubes could be used to take a direct measurement at that point. The percent of isokinetic at which the gas samples were drawn from both the stack and combustion zone sampling sites was calculated from the following equation given in EPA Method 5:

$$I = \frac{\left(1.677 \frac{\text{min}}{\text{sec}}\right)\left[\left(0.00267 \frac{\text{in. Hg-cu ft}}{\text{ml -°R}}\right) V_W + \frac{V_M}{T_M}\left(P_{Bar} + \frac{\Delta H}{13.6}\right)\right] T_s}{eV_s P_s \left(\frac{0.7854\ D_n^2}{144}\right)}$$

The terms of this equation are defined and values measured for each test burn are summarized in Table B-1. It was assumed for the purpose of these calculations that the 0.5-inch diameter combustion zone probe would behave roughly the same as a 0.5-inch nozzle.

Tables B-2 and B-3 summarize the sample gas and collected water volume data, respectively. The gas volumes are corrected to standard conditions and are given for both the wet and the dry gas streams. The wet gas volumes include water vapor. Dry gas volumes were used only to calculate grain loadings for EPA Method 5. All other calculations of species concentrations in the sampled gas were performed with the wet (or true) gas volumes.

Table B-1. Sampling System Data Summary

Run/Train	Sampling Time e(min)	Gas Volume V_m (ft^3)	Liquid Volume V_w(ml)	Stack Temp. T_s(^oF)	Dry Gas Meter Temp. T_m(^oF)	Nozzle Diameter D_n (in.)	Gas Velocity V_s(ft/sec)	Barometric Pressure P_{Bar}(in. Hg)	Stack Pressure P_s (in. Hg)	Pressure Drop ΔH (in. H_2O)	Percent Isokinetic
Run I											
Stack	100	56.1	896	155	82	0.5	14.5	30.08	30.10	0.9	95
Combustion Zone	135	106.9	265	1650	89	*	34.8	30.08	30.34	1.5	120
Run II											
Stack	60	35.5	321	150	82	0.5	12.6	29.84	29.86	1.4	93
Combustion Zone	180	181.1	186	1460	95	*	40.7	29.84	30.15	3.5	110
Run III											
Stack	60	30.1	283	130	74	0.5	11.5	30.49	30.51	1.0	85
Combustion Zone	173	138.4	285	1414	84	*	40.7	30.49	31.01	2.0	90
Run IV											
Stack	60	46.0	398	140	86	0.5	16.0	30.20	30.22	2.2	92
Combustion Zone	180	181.4	504	1515	102	*	41.1	30.20	30.66	3.5	120
Run V											
Stack	60	60.1	648	160	90	0.5	28.9	30.02	30.04	4.1	74
Combustion Zone	163	139.8	341	1550	100	*	41.8	30.02	30.45	2.5	100

*No nozzle was used for the combustion zone sampling train.

Table B-2. Systech Sample Gas Volumes at Standard Conditions

Test No.	Stack				Hot Zone			
	Dry		Wet		Dry		Wet	
	ft^3	m^3	ft^3	m^3	ft^3	m^3	ft^3	m^3
I	55.15	1.56	97.62	2.76	103.75	2.94	116.31	3.29
II	34.66	0.98	49.88	1.41	172.48	4.88	181.28	5.13
III	30.44	0.86	43.85	1.24	137.41	3.89	157.05	4.45
IV	47.32	1.34	75.64	2.14	172.67	4.89	196.54	5.57
V	58.11	1.65	88.80	2.51	132.75	3.76	148.89	4.22

Table B-3. Collected Water Volume Data

Test	Water Volumes in Impingers								
	1st Imp. (ml)		2nd Imp. (ml)		3rd Imp. (ml)		4th Imp. (g)		Total Liquid Sample (ml)
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	
I Hot Zone	100	295	100	135	-	10	-	25.2	440
Stack	100	380	100	355	-	325	-	35.6	1060
II Hot Zone	100	200	100	135	-	10	-	40.6	345
Stack	100	350	100	160	-	2	-	9.3	512
III Hot Zone	100	325	100	227	-	15	-	47.3	567
Stack	100	305	100	160	-	10	-	7.9	475
IV Hot Zone	100	295	100	297	-	60	-	51.6	652
Stack	100	267	100	283	-	35	-	12.5	585
V Hot Zone	100	363	100	143	-	3	-	31.5	509
Stack	100	345	100	362	-	115	-	25.5	822

APPENDIX C

CALCULATION OF WASTE DESTRUCTION PERFORMANCE

The waste destruction performance data presented in Table C-1 were calculated for the four runs where waste was actually burned, that is, there is no data for the fuel oil background run, SY-II. Input into these calculations was taken from several other sources in this report and the locations of the sources are indicated in the example below.

The waste destruction efficiency (DE_{waste}) is based upon comparing a waste input rate to a waste emitted rate.

$$DE_{waste} = \frac{\text{waste input} - \text{waste emitted}}{\text{waste input}} \times 100\% \qquad \text{(C-1)}$$

Equation (C-1), restated in another form, is

$$DE_{waste} = \frac{I_{waste} - [VFR_{gas}\ E_{waste}]}{I_{waste}} \times 100\% \qquad \text{(C-2)}$$

where:

I_{waste} = input rate of organic portion of aqueous waste feed, milligrams per second.

VFR_{gas} = volumetric flow rate of combustion gases from the reactor, cubic meters per second. It is the sum of the fluidizing air, the overbed air and the water vapor from the aqueous waste (from Table 5-1).

E_{waste} (mg/m^3) = concentration of organic waste constituents in combustion gas as determined by GC (the sum of the resultant concentrations for the three samples from eacn run (Table 5-3).

Similarly the destruction efficiency for total organics ($DE_{total\ organics}$) compares the input rate of combined waste and auxiliary fuel to the emitted rate of all organic material found in the combustion zone samples.

$$DE_{total\ organic} = \frac{I_{fuel} - [VFR_{gas}\ E_{total\ organics}]}{I_{fuel}} \times 100\% \qquad \text{(C-3)}$$

where:

I_{fuel} = input rate of organic portion of waste plus fuel oil (when used). Calculated from the data in Table 5-1. Units are milligrams per second.

$E_{total\ organics}$ = sum of the concentrations of all organics found in the combustion zone samples. (Tables 5-5, 5-6, 5-7) Units are milligrams per cubic meter.

The calculation for test number SY-I is presented below as an example. Initially I_{waste} is calculated, then VFR_{gas}, and finally E_{waste} is added to Equation (C-2) to calculate DE_{waste}.

$$I_{waste} = 49.9\ \ell/\text{min}\ \frac{\text{min}}{\text{60-sec}} \times 1.062 \times 10^{6}\ \text{mg}/\ell \times 0.082 = 72{,}000\ \text{mg/sec}$$

where:

49.9 min = aqueous waste feed rate (Table 5-1)

$\frac{\text{min}}{\text{60 sec}}$ = minutes to seconds conversion

1.062 = specific gravity of aqueous waste at 15°C (dimensionless)

0.082 = weight fraction of waste constituents in waste (dimensionless)

VFR_{gas} = fluidizing air + overbed air + water vapor

$$= \left[340\ \frac{m^3}{min} + 72\ m^3/min + 49.9 \times \frac{1000g}{l} \times 1.062 \times\right.$$

$$\left. X0.86\ \frac{gH_2O}{g} \times \frac{mole\ H_2O}{18\ g\ H_2O} \times \frac{0.024\ m^3}{mole}\right] \frac{min}{60\ sec}$$

$$= \left[\frac{348\ m^3}{min} \times \frac{72\ m^3}{min} \times \frac{61\ m^3}{min}\right] \frac{min}{60\ sec}$$

$$= 8.0 \frac{m^3}{sec}$$

where:

340 and $\frac{72\ m^3}{min}$ = air feed rates (Table 5-1)

$49.1 \frac{l}{min}$ = waste feed rate (Table 5-1)

1.062 = specific gravity of waste at $150^{o}C$ (Page 4-2)

$0.86 \frac{gH_2O}{g}$ = water content of waste (Page 4-2)

$\frac{0.024\ m^3}{mole}$ = approximate molar volume of water vapor at atmospheric pressure and $21^{o}C$.

Calculation of DE_{waste}

$$DE_{waste} = \frac{72{,}000 \frac{mg}{sec} - \left(\frac{8.0\ m^3}{sec} \times 0.03 \frac{mg}{m^3}\right)}{72{,}000 \frac{mg}{sec}} \times 100\% = 99.9997\% \qquad (C-3)$$

The destruction efficiencies for total organics, $DE_{total\ organic}$ are calculated in a similar manner using equation C-3 and inputing the combined waste and auxiliary fuel feed and the concentration of total organics found (Tables 5-5, 5-6 and 5-7).

APPENDIX D

ANALYTICAL CHEMISTRY DETAILS

This appendix consists of additional discussion of the organic analysis test results presented in Section 5. The discussion deals with the details of the IR and LRMS data interpretation related to the various survey analysis residues from the sample extracts. The preparation of these residues is discussed in Section 4. The results of these interpretations are presented in Section 5. Sections D.1 through D.5 discuss the survey results of the following sample forms in respective order:

- Combined probe wash and filter extracts, D.1
- Sorbent trap extracts, D.2
- Scrubber water extracts, D.3
- Fluidized sand bed extracts, D.4
- Representative samples of the phenol and methyl methacrylate wastes, D.5

D.1 Combined Probe Wash and Filter Extracts (PF and PW)

The following paragraphs describe the results of the survey analyses performed on the residues of the subject concentrated extracts. The amounts of organic residue obtained from careful evaporation of a 2 cc aliquot of organic concentrate are presented in Table 5-5. The amounts shown have been corrected for control samples involving extraction of precleaned thimbles and evaporation of the unused solvent. The amounts recovered in the blanks represent from 2 to 17 percent of the total weight obtained.

The infrared spectra of these samples indicated by the relative intensities of key peaks that the major constituents were aliphatic hydrocarbons. The presence of an ester at moderate levels or higher is also indicated. The presence of silicone oil or grease in varying amounts is shown by the spectra. The spectra for these samples were all exceedingly similar, thus indicating that the major constituents of these residues were the same. Band assignments for typical spectra is shown in Table D-1.

Low resolution mass spectra (LRMS) were obtained on three of these residues:

(1) SY-I-CG-PF+PW (phenol waste test)

(2) SY-II-CG-PF+PW (fuel oil background)

(3) SY-IV-CG-PF+PW (methylmethacrylate waste test).

Table D-1. IR Data for Probe Wash and Filter Extract Survey Residues

Maximum Absorbance (Frequency in CM^{-1})	Assignment
2970, 2950, 2850	δ-CH_3, δ-CH_2
1740	-C=O, ester
1470	-CH_2-scissor and asym bending -CH_3
1380	sym. bending -CH_3
1265	asym. C-O-C stretch
1120 to 1020	Si-O-Si stretch and sym. C-O-C stretch
800	Si-CH_3 rocking

The interpreted mass spectra are summarized as follows:

- The SY-I-CG-PF+PW sample contained hydrocarbon oils and phthlate esters as major constituents of the residue. A trace of silicones was also seen.
- The SY-II-CG-PF+PW sample contained hydrocarbon and phthalate esters. Di-tert-butylmethylphenol (BHT), silicones, and di-tert-octylresorcinol were found at minor levels in the extract.
- The SY-IV-CG-PF+PW sample contained hydrocarbons and silicones as major components, phlhalates at moderate levels and di-tert-butylmethyl phenol at a minor level.

These residues contain the same major constituents whose source is believed to background artifacts.

D.2 Sorbent Trap Extracts (ST)

This section provides some of the details of the survey analysis performed on the sorbent trap extracts in pentane and methanol. Analyses performed include residue weight, IR, and LRMS. The amounts of low volatile residue in the extracts are presented in Table 5-6. The details of the other analyses are presented below.

The IR spectra of the pentane extracts were essentially the same with the exception of changes in relative intensity of some peaks. The spectra indicate hydrocarbons, some esters and silicones whose source could have been lubricants or processing aids in the resin. The reason for this belief is that these materials are present in all samples including the control (unused) traps but are absent in the pentane and methanol solvent blanks. The amounts of these materials are larger in the residues from the actual sample traps (Table 5-6) suggesting that the test traps did indeed pick up some of these materials during the sampling or because of their use, release more of this material. There was no evidence of either phenol or methyl methacrylate monomer or waste constituents in the respective test samples nor in the extract residues from the two "doped" sorbent traps with known added amounts of these materials. This is not surprising since these relatively volatile materials added in milligram quantities to the traps, and already found in the extracts by GC were likely to be lost in the evaporation. (These survey procedures are not the prime methods for specific, expected waste constituents. The added phenol and MMA were found in the gas chromatographic analysis of the same extracts discussed earlier.

The IR spectra of the concentrated methanol extract residues indicated that similar materials were extracted from all the traps. The quality of the spectra from the methanol extracts is poorer since traces of the methanol solvent are in the residue and interfere. Evidence of hydrocarbons and esters are present. There was no evidence of phenol or methyl methacrylate in the respective IR spectra, nor were there any traces of these compounds in the "doped" sorbent traps. Again, this is not surprising due to their volatilities. Band assignments made for these data are given in Table D-2.

TABLE D-2. IR Assignments for Sorbent Trap Extract Survey Residues

Absorbance Maximum (Frequency, cm^{-1})	Assignment
2970, 2950, 2870	Aliphatic Hydrocarbons
1740	ester, C=0
1670	
1460	Assym. bending of $-CH_3$ or $-CH_2$ scissor
1380	methyl
1260	Asym. C-0-C stretch
1050 1020	Sym. C-0-C stretch
800	Si $-CH_3$ rocking

Inspection of the low resolution mass spectra of the residues obtained from mild evaporation of sorbent trap extract residues provided data which confirm the observations made on the IR. The types of compounds in the residues included major amounts of hydrocarbons, and phthalate esters. Fatty acids or long chains hydrocarbons with several carboxylic acid groups were also present. The LRMS data were searched for evidence of the components of the waste feed but no such evidence was found. In addition the data were searched for possible partial decomposition, pyrolysis products or secondary combustion products such as POM but, again, nothing was detected.

Some general observations on the behavior of the traps was also obtained from these analyses.

- There does not appear to be any preferential extraction of any one type of these materials by either pentane or methanol. However, methanol is shown to be more effective in extracting larger amounts of these compounds.
- These compounds still appear to be found in the resins in spite of the intensive extraction and clean up procedures used as described in Section 4. Based on our experience with the traps from the tests at the Marquardt Company (Facility One), methylene chloride was added to the solvents used in sequential extraction of the resin prior to use. Its use has not solved this mild contamination problem which to the analyst is annoying, but does not present any serious detrimental impact on the analysis of samples.

The mass spectral pattern discussed below is typical of the LRMS data taken from all the sorbent trap extract residues in pentane and methanol. It is stressed that this is low resolution mass spectrometer analysis of a mixture and several compounds present may contribute to a specific spectral pattern. Therefore, specific compounds present may not be determined with any real confidence. However the classes of compounds do become quite apparent as shown in Table D-3.

TABLE D-3. LRMS Assignments for Sorbent Trap Extract Survey Residues

Peak Pattern	Assignments
27, 29, 41, 43, 44, 55, 57, etc. increasing by 14 AMU beyond 300 AMU	Alkanes and olefins, either as compounds or as substitutes of compounds
66, 73, 147	Silicones*
70, 81, 95, 109, 121, 123, 137	Believed to be squalene, $C_{30}H_{50}$
149*	Phthalate esters
205, 223, 236, 278	Butyl phthalate ester

*Not found in all samples

D.3 Survey Analysis of Scrubber Water Extracts

Samples of the wet scrubber's recirculating water were taken before each test when the scrubber system had been previously drained and filled twice with city water. At the completion of each test a sample of the used scrubber water was taken. These samples were designated FSW (fresh scrubber water) and SSW (spent scrubber water), respectively. These samples were extracted and analyzed per the procedures described in Section 4.4.

The results of the gravimetric portion of the survey analysis of these samples is summarized in Table 5-14. The IR spectra of these samples were essentially identical and indicate hydrocarbon oils and esters of phthalic acid. These materials are commonly used as lubricants and also as plasticisers in polymeric materials. It is not surprising that these materials are present in a scrubber since the several pumps and valves in the facility must be lubricated. These spectra were also searched for any evidence of the constituents found in the representative wastes. No evidence of any of these species was found. The Table D-4 presents the IR spectral band assignments for the residue of the scrubber water extracts.

Table D-4. IR Assignments for Scrubber Water Extract Survey Residues

IR Absorption Maximum (frequency in cm^{-1})	Assignment
2980, 2940, 2870	C-H stretch, aliphatic hydrocarbons
1730	C=O stretch
1460, 1380	Asymetric and symetric $-CH_3$ bending
1260	=C-O-C symetric stretching (ester)
1120	=C-O-C symetric stretching (ester)
1080	Orthosubstuted phenyl

The low resolution mass spectral (LRMS) data confirm the conclusions made from the IR data. Selected sample residues were analyzed and the data indicate the presence of phthalates and hydrocarbon oils. Azelaic acid (nonanedioc acid) or its esters are also believed to be present as a minor constituent(s). The spectral pattern of Table D-5 is typical of the very similar pattern which these samples exhibited.

The phenol, methlmethacrylate, benzenes, toluenes and cresols originally detected in the two wastes were specifically searched for in the LRMS of the residues. They were not detected in the LRMS data nor was there any evidence of toxic by-products.

Table D-5. LRMS Assignments for Scrubber Water Extract Residues

Spectral Pattern (Atomic Mass Units. AMU)	Assignment
27,29,41,43,55,57,69,71,83, 85,97,99	Typical pickett pattern from normal and branched aliphatic and olefinic hydrocarbons
70,112,171 plus portions of the pickett pattern above.	Believed to be azelaic acid and/or its esters
149,167,185 plus portions of the pickett pattern above	phthalic acid and/or its esters

D.4 Fluidized Sand Bed Extracts

The samples of the sand bed, which were taken after each test, were extracted with pentane and given the standard survey analyses. The results of the gravimetric analyses are presented in Table 5-17. Parts per million quantities of a residue were found in the extracts. The control samples for this procedure did not yield enough of a residue to be weighed, thus there are no background contributions. The IR spectra for these residues are essentially all the same and indicate hydrocarbon oils/greases as the primary constituent of these small residues with the distinct possibility of an ester and silicones being present. The IR band assignments for a typical spectra are presented in Table D-6.

Table D-6. IR Assignments for Sand Bed Extract Survey Residues

Maximum Absorbance (frequency in cm^{-1}	Assignment
2970, 2940, 2870	δ C-H
1740	C=O stretch
1460	δ C-H
1380	$-CH_3$
1260	asym. C-O-C stretch
1100	Si-O-Si
1020	sym. C-O-C stretch and Si-O-Si
800	Si $-CH_3$ rocking

Two survey samples were selected using IR, as being typical of all the sand extracts. These two samples were subjected to LRMS analysis to confirm the IR data.

The sand residue extract from SY-I (from a phenol waste test) contained hydrocarbon oils as the major constituent of the evaporated extract residue. Di octyl phthalate was present at a moderate level. Minor amounts of di-tert-butyl methyl phenol (also known as BHT, an antioxidant), and methyl abietate, a wood resin derivative possibly coming from the extraction thimbles, were also seen. An incompletely identified chlorinated, substituted aromatic (apparent molecular weight 228) was also seen at minor levels. Its source is unknown.

The other sand extract that was examined by LRMS was from SY-IV. This sand sample was from a test with methyl methacrylate waste. Compounds found in the residue included hydrocarbon oils (major), phthalates and fatty acids (moderate) and di-tert-butyl methyl phenol (minor). The unknown chlorinated aromatic (MW228) was also present at minor levels. There was no evidence in the spectra of the silicones seen in their spectra.

These materials are believed to be more examples of the low level contamination of samples by these ubiquitous organics which can occur during even the most carefully controlled sampling and analysis procedures. It is not believed that these materials come from the sand bed itself, which when taken from the fluidized bed incinerater, is hot to a cherry red color and which has been standing for as much as one half hour after all fuel flow has stopped. Trace contamination during sample acquisition, storage, preparation and analysis is believed responsible. No further work was done to identify the source(s) of these materials other than to stress awareness of the problem of contamination as it applies to all procedures and operations.

D.5 LRMS Survey of Representative Phenol and MMA Wastes

The LRMS data on the representative sample of the phenol waste were obtained by using the direct solids probe technique on the same residue from evaporation of the waste used in the IR. The interpreted spectra is summarized in Table D-7. At the lower probe temperature of 150°C the major constituents were phenol, cresol isomers, and aliphatic hydrocarbon oils. Phthalates were present at minor to moderate levels. There was also a very strong peak at m/e 74. This peak frequently occurs in the fragment pattern of methyl esters of various different carboxylic acids with a wide range of molecular weights. The other class of compounds suggested by this intense peak are sulfur containing hydrocarbons such as sulfides, dithianes, and trithianes. The spectrum from the same sample at a probe temperature of 250°C had increased peak intensities at the higher molecular weight end of the spectrum. The same m/e 74 peak is easily the most intense peak. Other strong peaks are apparent as indicated in Table D-7. The point is stressed that in this survey type analysis, several compounds may contribute to a particular peak pattern in the spectrum. The resulting interpretation and assignments in Table D-7

Table D-7. LRMS Assignments of Representative Phenol Waste (Water Removed)

Mass Spectral Pattern (AMU)	Assignment
27,29,41,43,55,57, increasing by 14 AMU 74	Hydrocarbons either as oils or substituents on other molecules, major Methyl esters, sulfurhydrocarbons, major
39,50,51,53,65,66,94	Phenol, major
27,51,53,77,79,107,108	Cresols, major
149,167,223	Phthalates, minor
77,107,108,121,122	Ethylphenol or dimethyl phenol, minor
208	Possible anthraquinone, or methoxyphenanthrene, minor
65,66,139	Nitro phenol, minor
245,246,247	Possible di-phenylphenol or 2 Biphenylphenyl ether., minor
74,228	Possible methyl-n-tridecanoate, minor
185	Possible sebacic acid compounds, minor
256	Relatively low intensity possibly a methyl substituted benzantracene or Benzo phenanthrene.
274,275	Not assigned, minor
287,288	Not assigned, minor
302,303	Not assigned, minor

cannot always be confirmed. The available literature on standard mass spectra of the sulfur compounds mentioned above is some what limited. However, without literature confirmation, it is believed that some of the unidentified minor constituents in the table may be part of this class of sulfur containing compounds whose presence is indicated by the very intense 74 AMU peak. It should be pointed out that these unidentified higher molecular weight compounds are minor constituents in the phenol waste. LRMS at 400°C did not reveal any additional spectral features not found at 250°C.

The LRMS analysis of the MMA representative waste, after water and MMA removal by evaporation, indicated primarily hydrocarbon oils with minor or trace levels of esters, fatty acids, etc., (Table D-8). Peaks at 252,253 AMU suggest the presence of a POM but no confirmation exists.

Table D-8. LRMS Assignments for Representative Methyl Methacrylate Waste (Water Removed)

Mass Spectral Pattern (AMU)	Assignment
41,43,55,57, etc., increasing by 14 AMU (CH_2) extending above 400 AMU	hydrocarbon oils with molecular weights greater than 400, major
149,167	Phthalate esters, minor
185	Adipates, sebecates, minor
211,225	Possible p-tertbutylphenyl phenyl ether, trace
252,253	Possible a benzpyrene, or a benzo fluoranthene, trace
309,323	Unassigned, trace

μσ1467b